Photoredox Photochemistry of Tris(dibenzyldithiocarbamato)iron(III)

Dwight P. Schwendiman and Jeffrey I. Zink*[1]

Contribution No. 3561 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received November 18, 1975*

Abstract: Tris(dibenzyldithiocarbamato)iron(III) is photoactive in halogenated hydrocarbon solvents. The photoproducts in chlorinated and brominated hydrocarbons are five-coordinate chloro- and bromobis(dithiocarbamato)iron(III), respectively. The photoreaction is both wavelength and solvent dependent. The lowest energy photoactive absorption band is assigned as a ligand to metal charge transfer, $\pi \rightarrow e_g^*$. The reactivity is interpreted in terms of a molecular orbital model. The quantum yields of the reaction qualitatively follow the carbon-halogen bond energies. The mechanism of the reaction involves formal photoreduction of the iron, homolytic iron-sulfur bond cleavage, and free radical halogen abstraction from the solvent.

The photochemistry, and in particular the charge transfer photochemistry, of iron complexes has not been extensively investigated.[2] The reported types of reactions which result from irradiating charge transfer bands include solvation (aquation of iron(II) cyanide complexes), photoelectron production (from $Fe(CN)_6{}^{4-}$), and photoreduction of iron(III) complexes (including the common actinometric system trisoxolatoferrate(III)).[2] In the specific case of ligand to metal charge transfer photochemistry, only a handful of systems have been surveyed and the usual photoprocess is reduction of iron(III) to iron(II).[2b]

Our interest in the possible photoreactivity of tris(dibenzyldithiocarbamato)iron(III), $Fe(Bz_2DTC)_3$, arose because of the photochromism expected by analogy with $Ni(Bz_2DTC)_3Br$.[3,4] Instead, an unexpected photoreaction, halogen abstraction from organic halide solvents to produce five-coordinate $Fe(Bz_2DTC)_2X$, was found. The reaction exhibits several unusual photochemical features. First, the photoreaction causes a change in the coordination number of the iron(III) with retention of the oxidation state. Second, the photochemical reaction is wavelength dependent and may occur from a specific spin state (the low spin doublet state) in a complex which exists in thermal equilibrium between two different spin states at room temperature.[5,6] Finally, the result of the photoreaction is chemical bond breaking in both the solvent and in the metal complex rather than the common metal-ligand heterolytic bond cleavage and concomitant metal solvation. In this paper, we report the photochemical mechanism, the excited state origin, and the solvent and wavelength dependence of the quantum yield of product formation of the photoreaction of $Fe(Bz_2DTC)_3$.[7]

Experimental Section

Preparation of Compounds. Potassium *N,N*-dibenzyldithiocarbamate,[8] tetrabenzylthiuram disulfide,[9] tris-*N,N*-dibenzyldithiocarbamatoiron(III),[6] bis-*N,N*-dibenzyldithiocarbamatoiron(III) chloride,[10] bis-*N,N*-dibenzyldithiocarbamatoiron(III) bromide[11] and tris-*N,N*-dibenzyldithiocarbamatoiron(IV) tetrafluoroborate[12] were synthesized by literature methods. Anal. Calcd for $C_{15}H_{14}NS_2K$: C, 57.83; H, 4.54. Found: C, 57.74; H, 4.72. Calcd for $C_{45}H_{42}N_3S_6Fe$: C, 61.90; H, 4.86. Found: C, 62.10; H, 4.70. Calcd for $C_{30}H_{28}ClN_2S_4Fe{\cdot}O{\cdot}6CCl_4$: C, 50.45; H, 3.88. Found: C, 50.55; H, 4.01. Calcd for $C_{45}H_{42}BF_4N_3S_6Fe$: C, 56.30; H, 4.42. Found: C, 57.21; M, 4.46.

Instrumentation. The electronic absorption spectra were taken using both Cary 14 and Cary 15 spectrometers. A Hitachi Perkin-Elmer 139 uv-visible spectrophotometer was used to measure absorbance changes in the quantum yield and rate studies. The mass spectra were taken on an AEI MS-9 spectrometer, the NMR spectra on a Varian A-60-D spectrometer, and the EPR spectrum on an E-12 spectrometer. All quantum yield studies were done on an optical bench using a Hanovia 1000-W Hg-Xe lamp. The 3341, 3660, 4053, 4358, 5461, and 5770 Å Hg lines were isolated using filters described in the literature[13] with the following changes. For all filters requiring a Pyrex plate, a Pyrex lens (Abs > 1 at λ <325) was used for the high energy cutoff. The 3660 Å line was completely eliminated from the 3341 Å line by the addition of a 1-cm solution filter of a saturated solution of *N*-(5-dimethylamino-3-methylpentadienylidene)diethylammonium perchlorate.[14] For the 3660 Å line, a Corning filter No. CS 7-39 was used in place of No. CS 7-37. For the 4053 Å line, a Corning glass filter, No. GG-13, was added to improve the elimination of the 3660 Å line. For the 4358 Å line, a Gena filter No. WG-2 was added to eliminate the 3% transmittance at 3200–3600 Å. Purity of the spectral line was determined using a Jarrell-Ash 0.25 M monochrometer calibrated with a low pressure mercury source. The relative photochemical rate studies were carried out using a Hanovia 450-W quartz Hg vapor lamp operated at 100 W and a merry-go-round. A Pyrex glass tube (4 in. diameter, Abs > 1 at λ <300 nm) was placed around the quartz lamp holder to filter out the high energy uv irradiation. The full spectral range of wavelengths greater than 300 nm was used to ensure maximum intensity in the photoactive band. The lamp and samples were kept at constant temperature by placing the merry-go-round in a water bath and circulating cooled water through copper tubing around the outside of the bath.

Kinetic Studies. The kinetics of the photoredox halogen abstraction reaction were obtained using the merry-go-round apparatus. The change in concentration of the $Fe(Bz_2DTC)_3$ was measured by monitoring the increase in the absorbance of the 615-nm line for those solvents in which an isosbestic point is observed. For those solvents in which no isosbestic point was observed (vide infra), the $Fe(Bz_2DTC)_3$ and $Fe(Bz_2DTC)_2Cl$ concentrations were spectrophotometrically determined at wavelengths greater than 400 nm where there is no interference by the absorptions of other species. A starting concentration of approximately 2.4×10^{-4} M gave easily measurable concentration changes. All solvents were purified by distillation before use.

The intensity dependence studies were done on an optical bench rather than the merry-go-round. The intensity of the 3341-Å Hg line was varied using neutral density filters.

Quantum Yields. The quantum yields were determined by following changes in the electronic absorption spectra. The samples were housed in a thermostated block at room temperature under the same geometrical restraints as the actinometer solutions. The light intensity was determined by ferric oxalate actinometry.[13] The number of photons absorbed was calculated taking into account the inner filter effect.[15] All quantum yields were measured at less than 20% of the total reaction time.

Results

1. Photoinduced Halogen Abstraction. During irradiation, a solution of brown $Fe(Bz_2DTC)_3$ in $CHCl_3$ changes color to a very intense forest green due to the appearance of an absorption band at 625 nm. An isosbestic point is observed at 430 nm. The green photoproduct, chlorobis-*N,N*-dibenzyldithiocarbamatoiron(III), $Fe(Bz_2DTC)_2Cl$, was identified by comparing its electronic absorption and NMR spectra with

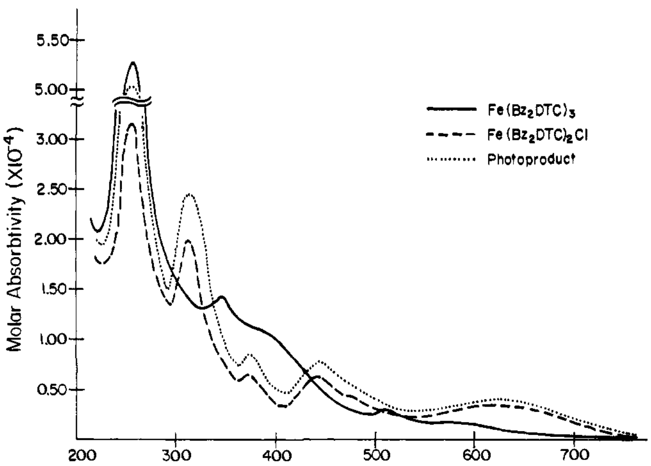


Figure 1. Uv-visible spectra of Fe(Bz$_2$DTC)$_3$, Fe(Bz$_2$DTC)$_2$Cl, and the photoproduct in chloroform. The spectrum of the photoproduct is offset slightly from that of Fe(Bz$_2$DTC)$_2$Cl to facilitate comparison of the two spectra.

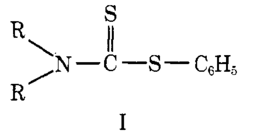
those of the pure compound. The electronic absorption spectra of Fe(Bz$_2$DTC)$_3$, Fe(Bz$_2$DTC)$_2$Cl, and the green photoproduct are shown in Figure 1. The proton NMR spectrum of the pure five-coordinate complex has peaks at 26.25, 7.98, 7.10, and 1.08 ppm. relative to Me$_4$Si. The peaks at 7.98 and 1.08 ppm are well separated from those of the six-coordinate Fe(Bz$_2$DTC)$_3$ starting material and the salt of the free ligand. The NMR spectrum of the photoproduct showed new peaks at 7.98 and 1.08 ppm, thus confirming its identification as Fe(Bz$_2$DTC)$_2$Cl.

Similar spectral changes occur when CH$_2$Br$_2$ is used as the solvent. The intense characteristic band appears at 630 nm for the five-coordinate bromide complex, Fe(Bz$_2$DTC)$_2$Br, with ϵ 3.34 × 10^3 M^{-1} cm^{-1}, slightly less intense than that of the chloro complex.

Tris-*N*,*N*-dibenzyldithiocarbamatoiron(IV) tetrafluoroborate is also photoactive in CHCl$_3$ or CH$_2$Cl$_2$ when irradiated with unfiltered white light (λ >325 nm). The spectrum of the green photoproduct is identical with that of Fe(Bz$_2$DTC)$_2$Cl shown in Figure 1.

Both Fe(Bz$_2$DTC)$_2$Cl and Fe(Bz$_2$DTC)$_2$Br undergo secondary photolysis to give pale orange solutions. This photoreaction is much more efficient for Fe(Bz$_2$DTC)$_2$Br than for Fe(Bz$_2$DTC)$_2$Cl. The electronic absorption spectrum of the photoproduct of Fe(Bz$_2$DTC)$_2$Br shows two intense bands at 393 and 475 nm (ϵ 4000 M^{-1} cm^{-1}) compared to only one band at 360 nm for the photoproduct of Fe(Bz$_2$DTC)$_2$Cl. The photodecomposition products of Fe(Bz$_2$DTC)$_2$Cl and Fe(Bz$_2$DTC)$_2$Br were not further characterized because secondary photolysis is minimized by using short irradiation times.

We have not completely studied the reactions of the photolabilized dithiocarbamate ligand. Recent studies by Pignolet using unfiltered light have shown that at least 88% of the ligand product in the chlorine abstraction from chlorobenzene by tris-*N*,*N*-diethyldithiocarbamatoiron(III) is a thio ester with structure I.[16] Small amounts of 2-chlorobiphenyl, 4-chlorobiphenyl, biphenyl, and tetraethyl thiuramdisulfide were also found.[16]



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2. The Quantum Yield of the Photoinduced Halogen Abstraction Reaction. The quantum yield of the photoinduced halogen abstraction reaction of Fe(Bz$_2$DTC)$_3$ is wavelength and solvent dependent. The photoactivity of Fe(Bz$_2$DTC)$_3$ was quantitatively investigated at 334, 366, 405, 436, 546, and 577 nm. The photoreaction was only observed upon irradiation of the complex's 348-nm absorption band and those higher in energy. The rate of the photoreaction increased at the shorter wavelengths. Quantum yields were not measured at shorter wavelengths because of the interference caused by solvent absorption in some of the solvents used.

Table I. The Solvent Dependence of the Quantum Yields of the Photoredox Reaction of Fe(Bz$_2$DTC)$_3$ at 334 nm

Solvents	Φ(disappearance)	Φ(appearance)	Bond energy kcal/mol
CH$_2$Br$_2$	0.14 ± 0.01	0.14 ± 0.02	62.5[c]
CCl$_4$[a]	0.10 ± 0.02	0.10 ± 0.02	68[d]
CHCl$_3$	0.048 ± 0.004	0.048 ± 0.004	71.5[e]
CH$_2$Cl$_2$	0.0076 ± 0.0015	0.0080 ± 0.0009	75[e]
ClC$_6$H$_5$[b]	0.0087 ± 0.0031	0.0045 ± 0.0015	86[f]
p-ClC$_6$H$_5$-OC$_2$H$_5$[b]	0.0095 ± 0.0012	0.005 ± 0.0009	
Benzene	0.002 ± 0.0004		

[a] 9.33 M solution in benzene. [b] 3.21 M solution in benzene. [c] Reference 29. [d] Reference 13, p 824. [e] P. Goldfinger and G. Martens, *J. Chem. Soc.*, 2220 (1961). [f] R. T. Morrison and R. N. Boyd, "Organic Chemistry", Allyn and Bacon, Boston, Mass., 1970, p 46.

The appearance and disappearance quantum yields of Fe(Bz$_2$DTC)$_3$ in a series of halogenated methanes and substituted chlorobenzenes are given in Table I. The ordering of the appearance quantum yields qualitatively follows the ordering of the C-X bond energies. Because of extremely rapid thermal reactions, no photochemical reaction can be measured in bromoform or carbon tetrabromide. The rate of the thermal reaction in CBr$_4$ is faster than in CHBr$_3$ and thus also parallels the carbon-halogen bond strength. Above 50 °C, a thermal reaction is also observed in dibromomethane and CCl$_4$.

In the absence of halogen containing compounds, Fe(Bz$_2$DTC)$_3$ undergoes photochemical decomposition with low quantum yields. The electronic absorption spectrum after 80% decomposition has only one band with ϵ >10^4 (at λ_{max} 267 nm). The molar absorptivity of the decomposition product is less than 10% of that of Fe(Bz$_2$DTC)$_3$ and Fe(Bz$_2$DTC)$_2$Cl at λ >400 nm. The disappearance quantum yield for the photodecomposition of Fe(Bz$_2$DTC)$_3$ in neat benzene is given in Table I for 348-nm irradiation. The wavelength dependence of this reaction was not studied. Doubling the concentration of Fe(Bz$_2$DTC)$_3$ from 2.3 × 10^{-4} to 4.5 × 10^{-4} M increases the rate of the decomposition reaction by a factor of 1.8. Approximately 100% of the incident light is absorbed at both concentrations. The same photodecomposition reaction is observed in toluene, cyclohexane, acetone, and acetonitrile with rates relative to those in benzene of 1.2, 1.1, 2.4, and 0.53, respectively. No reaction is observed in methanol. In contrast to the halogen abstraction reaction, the photodecomposition does not begin immediately upon the start of irradiation. The absorption spectrum of Fe(Bz$_2$DTC)$_3$ begins to decrease after approximately 3 min irradiation time at 3 × 10^{16} photons/s incident intensity in all of the above solvents except acetonitrile. In acetonitrile, the required "induction period" is 24 min at the same intensity. Because this photodecomposition reaction represents a minor pathway compared to halogen abstraction, it was not studied further.

The quantum yield of the abstraction of chlorine from chloroform at 23 °C is independent of the incident light intensity. The intensity was varied by 2 orders of magnitude in five steps using neutral density filters. The reaction is thus definitely a one photon process.

3. Mechanism of the Photoreaction. Addition of tetrabenzylthiuram disulfide (thiuram) to a solution of $Fe(Bz_2DTC)_3$ in chloroform results in the retarding of the photoinduced chlorine abstraction. The 430-nm isosbestic point is not affected by the addition of the thiuram up to a 10:1 thiuram/$Fe(Bz_2DTC)_3$ ratio. A further increase of the concentration of the thiuram totally inhibits the formation of $Fe(Bz_2DTC)_2Cl$.

In contrast, addition of $K(Bz_2DTC)$ to solutions of $Fe(Bz_2DTC)_3$ in 1:1 chloroform/acetonitrile mixtures temporarily results in no net photochemical reaction for a specific length of time followed by normal reactivity. This "induction" period is directly proportional to the initial molar ratio of $K(Bz_2DTC)$ to $Fe(Bz_2DTC)_3$. KCl is formed stoichiometrically in a 1:1 molar ratio of KCl to $K(Bz_2DTC)$. The induction period is followed by the expected photochemical halogen abstraction reaction at its normal rate. The measured rates of chlorine abstraction following the "induction" period are independent of the initial $K(Bz_2DTC)$ concentration.

When the known radical reaction initiators benzoyl peroxide ($C_6H_5CH_2OOCH_2C_6H_5$) or triphenylmethyl chloride are added to a chloroform solution of $Fe(Bz_2DTC)_3$ in the dark, the halogen abstraction reaction occurs immediately. Addition of the reducing agent benzoin ($C_6H_5\,C(=O)C(OH)HC_6H_5$) also results in the thermal production of $Fe(Bz_2DTC)_2Cl$. A chloroform solution of the iron complex without benzoin is stable over the same period of time.

No production of $Fe(Bz_2DTC)_2Br$ is observed when mixtures of $Fe(Bz_2DTC)_3$ and $(n\text{-}Bu)_4NBr$ are irradiated in benzene, acetonitrile, acetone, or propylene carbonate. The higher dielectric solvents were used to minimize ion pairing of the ammonium bromide salt. Similarly, no photoreaction is observed in solutions of Me_4NCl in acetone and acetonitrile.

The reaction mechanism consistent with the above observations and the thioester product is shown in Figure 2. The photoexcited $Fe(Bz_2DTC)_3$ abstracts halogen radicals but does not react with halide ions. In addition the labilized dithiocarbamate ligand is lost as a neutral radical ligand and not as an anion. Any free anionic ligand undergoes a rapid thermal reaction with the photoproduced five-coordinate complex yielding the six-coordinate starting material.[10]

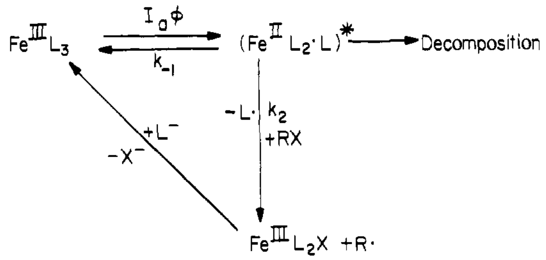

Figure 2. The reaction mechanism for the photoredox halogen abstraction by tris(dibenzyldithiocarbamato)iron(III).

Table II. Electronic Absorption Band Maxima and Assignments

λ_{max} $(Fe(Bz_2DTC)_3)$	λ_{max} $(Fe(Et_2DTC)_3)$	Band assignment $Fe(Et_2DTC)_3$[a]	
595	585	$\pi \rightarrow t_{2g}$	(ls)
510	508	$e_g \rightarrow \pi^*$	(hs)
385	389	$\pi \rightarrow t_{2g}$	(hs)
348	346	$\pi \rightarrow e_g$	(ls)
	286	$t_{2g} \rightarrow \pi^*$	(hs)
		$t_{2g} \rightarrow \pi^*$	(ls)
265	265	$\pi \rightarrow e_g$	(hs)

[a] Reference 20. The symbols ls and hs refer to low spin and high spin states, respectively.

Discussion

1. The Excited State Origin of the Photoredox Reaction. For the purposes of categorizing specific types of excited states with specific photochemical reactivity patterns of transition metal complexes, four types of orbitally designated excited states are convenient: ligand field (LF), metal to ligand charge transfer (MTLCT), ligand to metal charge transfer (LTMCT), and ligand localized (LL). The photoreactions originating from the LF excited states have been the most extensively studied.[2] The most common photoreaction is ligand labilization followed by solvation.[2] Detailed ligand field theoretical treatments of this type of photoreactivity have been presented.[17,18] In contrast, reactivities of the other types of excited states have been less extensively studied and interpreted. A common reaction from charge transfer states is photooxidation or reduction of the metal from the MTLCT and LTMCT states, respectively.[2] A thermodynamic treatment of the photochemical reactivity from these states has been proposed.[19] In this section, a molecular orbital explanation of the observed photoreactivity of tris(dibenzyldithiocarbamato)iron(III) is presented.

The electronic absorption band maxima of $Fe(Bz_2DTC)_3$ are listed in Table II together with those of $Fe(Et_2DTC)_3$ and the band assignments for the latter compound based on a molecular orbital calculation.[20] The proposed assignment treats the absorption spectrum as a superposition of the spectra of the high spin and the low spin complexes.[20] The two ground state configurations, ($^6A_1$ and $^2T_2$, respectively), exist in thermal equilibrium and are distinct on the electronic absorption time scale. On the basis of the similarity of the spectra of the diethyl and the dibenzyl derivatives, the excited states of the latter compound are assigned in the same manner as the analogous excited states of the former.

The quantum yield for halogen abstraction and formation of the five-coordinate $Fe(Bz_2DTC)_2X$ ($X^- = Cl^-, Br^-$) is strongly wavelength dependent. The reaction is observed only upon irradiating the bands at wavelengths of 348 nm and shorter. The photochemistry at wavelengths less than 325 nm was not quantitatively investigated because of the complication of light absorption by some of the solvents. The photoactivity within the investigated wavelength region can be assigned to the band at 348 nm and/or the shoulder of the 265-nm band.

The bonding changes caused by irradiating the 348- or 265-nm bands can be determined from the nature of the orbital populated (e_g^*) and the orbital depopulated (ligand π) in the one electron transition. The e_g^* orbital, primarily a linear combination of metal d_{z^2} and $d_{x^2-y^2}$, is antibonding with respect to the metal and the ligand sulfur atoms. Thus, populating this orbital would be expected to labilize the metal-sulfur bond. The ligand π orbital which is depopulated is primarily ligand S=C π bonding in character. Thus, depopulating this orbital would be expected to weaken the sulfur-carbon bonds. The bonding changes between the sulfur and the metal caused by depopulating this orbital are not as readily deduced, but in general loss of the ligand electron to form a neutral ligand radical would be expected to decrease the electrostatic attraction between the metal and the ligand. Furthermore, the electron transfer will formally reduce the iron(III) to iron(II) and further decrease the ligand-metal interaction. Thus, the net result of irradiating the $\pi \rightarrow e_g^*$ transition is expected to be metal-ligand bond weakening with concomitant metal reduction and ligand free radical formation.

The observed primary photoreaction is loss of a radical ligand and metal photoreduction in exact accord with the reactivity expected on the basis of the bonding changes. As has been previously suggested,[21,22] the interplay between spectroscopy, molecular orbital theory, and photochemistry can provide a means of simultaneously explaining photochemical reactivity and photochemically assigning excited states.

Two explanations for the photoinactivity of the bands assigned as CTTM $\pi \rightarrow t_{2g}$ are possible. First, populating the t_{2g} orbitals can only change the metal-sulfur π interactions. In ionic complexes, the metal-ligand π interactions are weaker than the σ interactions. The small changes in the metal-sulfur bond strength caused by populating the t_{2g} orbitals may not be sufficient to cause a photochemical reaction. Secondly, the lifetime of the excited $\pi \rightarrow t_{2g}$ excited state may be significantly smaller than that of the $\pi \rightarrow e_g{}^*$ excited state. In the former transition, the electron remains in an orbital of π symmetry while in the latter the electron populates an orbital which cannot participate in π interactions. Because the complex does not luminesce, the lifetime cannot be determined directly.

The molecular orbital interpretation of the photoactivity suggests that the band at 265 nm, assigned to the $\pi \rightarrow e_g{}^*$ transition of the high spin complex, should exhibit the same photoreaction as the 348-nm $\pi \rightarrow e_g{}^*$ transition in the low spin complex. Qualitatively, we found that the photochemistry of the higher energy bands give rise to the same photoproducts at a rate equal to or greater than that observed at 334-nm irradiation. However, the possibility of reactions from solvent excited states precludes quantitative comparisons or conclusions.

Because the photoreaction products are the same as those from the thermal reaction in CCl_4, CH_2Br_2, $CHBr_3$, CBr_4, and, in the presence of radical initiators, in $CHCl_3$ and CH_2Cl_2, the reaction could occur from the vibrationally excited ground state. The wavelength dependence of the photoreaction argues against this mechanism. If deactivation of the 348-nm state to the ground state occurs via the lower energy excited states, ground state vibrational excitation and reactivity would occur equally well when the lower energy bands are irradiated, contrary to experiment. The excellent correlation between the reactivity predicted from MO theory and that observed argues for an excited state reaction pathway. However, neither argument can definitely rule out the hot ground state mechanism.

2. The Solvent Dependence of the Quantum Yields. The effects of solvation on condensed phase transition metal photochemistry are poorly understood.[2] Recently, several papers have appeared which report studies of varying the solvent on the photoreactivities of metal complexes.[2,23,24] A specific solvent physical property which appears to be definitely implicated in influencing the photoreactivity is the viscosity.[24] In this section, we show that the solvent property which most strongly influences the reactivity of the halogen abstraction reaction is the carbon-halogen bond strength.

The solvent dependence of the appearance and disappearance quantum yields are given in Table I. The trend in the quantum yields of formation of the five-coordinate product roughly follows that in the C-X bond energies of the solvent halomethanes. The observed trend parallels the thermal rate of chlorine abstraction from halomethanes by Na·,[25] H·,[26] and CF_3·.[27,28] A similar trend is qualitatively observed in the rates of the thermal abstraction reaction in CBr_4 and $CHBr_3$. The bromine abstraction reaction is observed to be faster in CBr_4 than in CH_2Br_2, paralleling the C-Br bond energies of 49 and 56 kcal/mol, respectively.[29]

The ordering of the quantum yields does not follow that of the solvent molarity. The molarities are as follows: CH_2Br_2, 14.33 M; CCl_4, 8.40 M; $CHCl_3$, 12.43 M; and CH_2Cl_2, 15.73 M. Normalizing the quantum yield for equal molarity does not improve the correlation.

The carbon-halogen bond energy is not the only factor influencing the quantum yields of the photoinduced halogen abstraction reaction as is seen by comparing the quantum yields in CH_2Cl_2 and chlorobenzene. The C-Cl bond energy is greater in chlorobenzene than in CH_2Cl_2, but the appearance quantum yields in the two solvents are approximately equal. Other factors such as steric bulk, self association, hydrogen bonding, polarity, or solvating ability of the solvent could also affect the quantum yields. The relative importance of these various effects was not investigated. For a series of similar solvents, such as the halomethanes, these effects apparently remain essentially constant and the rate determining factor is the C-X bond strength.

The inequality of the appearance and disappearance quantum yields in the solvents with the highest C-X bond strengths is due to the additional photodecomposition reaction which does not involve halogen abstraction. Although the quantum yield of this reaction in benzene is small (0.002 ± 0.0004), it is of the same order of magnitude as the appearance quantum yields of $Fe(Bz_2DTC)_2Cl$ in CH_2Cl_2, ClC_6H_5 and p-$ClC_6H_4OC_2H_5$. The difference between the appearance quantum yield of $Fe(Bz_2DTC)_2Cl$ and the disappearance quantum yield of $Fe(Bz_2DTC)_3$ should equal the value of the quantum yield for the non-halogen abstraction decomposition reaction if there are no additional reaction pathways. These differences are 0.0047, 0.0042, and 0.0045 for CH_2Cl_2, C_6H_5Cl, and p-$ClCl_6H_4OC_2H_5$, respectively. Within the experimental error these values are nearly equal to the quantum yield of the decomposition reaction in benzene.

In CH_2Br_2, CCl_4, and $CHCl_3$, the quantum yield of the decompostion reaction is at least an order of magnitude smaller than the appearance quantum yields of $Fe(Bz_2DTC)_2Cl$. In these solvents, an isosbestic point is observed at 430 nm as expected if the appearance and disappearance quantum yields are equal.

3. Free Radical Reaction Pathway. The observed photochemical reaction of $Fe^{III}(Bz_2DTC)_3$ to form five-coordinate $Fe^{III}(Bz_2DTC)_2Cl$ could proceed via at least two pathways. First, reduction of the Fe(III) complex to a formal Fe(II) complex upon irradiation could result in homolytic cleavage of an Fe-S bond and the formation of a dithiocarbamate radical. The formation of $Fe(Bz_2DTC)_2Cl$ would occur by a reaction with a halogen radical. Secondly, if the photochemical excited state were a formal Fe(III) complex, heterolytic bond cleavage and formation of a dithiocarbamate anion could result and $Fe(Bz_2DTC)_2X$ would be formed by an annation reaction with ionic halide. However, the chemical evidence discussed below is consistent with only the radical reaction pathway.

No photoreaction is observed when $Fe(Bz_2DTC)_3$ is irradiated in the presence of $(n\text{-}Bu)_4NBr$ or $(Et)_4NCl$ in benzene, acetontrile, or propylene carbonate solutions. Thus, the photoexcited Fe complex does not react with the Br^- or Cl^- ions.

Additional evidence for the radical pathway is the different photochemical behavior observed upon the addition of potassium N,N-debenzyldithiocarbamate and tetrabenzylthiuram disulfide to chloroform solutions of $Fe(Bz_2DTC)_3$. Addition of the thiuram, which can undergo efficient dissociation into Bz_2DTC radicals,[30] slows the rate of the halogen abstraction. The presence of excess Bz_2DTC radicals causes the equilibrium to shift back toward $Fe(Bz_2DTC)_3$, thereby suppressing the formation of $Fe(Bz_2DTC)_2X$. At mole ratios of 50:1 thiuram to $Fe(Bz_2DTC)_3$, the abstraction of halide is completely suppressed. Addition of KBz_2DTC initially causes no net observable spectral changes to occur during irradiation. However, the cyclic reaction shown in Figure 2 is occurring during this time. The excess dithiocarbamate anion reacts with-$Fe(Bz_2DTC)_2Cl$ as rapidly as it is formed[10] to produce the starting iron species and Cl^- ions. No net build up of

$Fe(Bz_2DTC)_2Cl$ occurs until all of the excess ligand anion is reacted. The "induction" time of no observable product formation is quantitatively directly proportional to the salt concentration. The concentration of the Cl^- ions produced is equal to the initial concentration of the dithiocarbamate anion.

The reaction intermediate is depicted in Figure 2 as a "radical pair" consisting of a photoreduced iron(II) complex and a ligand free radical in order to emphasize the nature of the reaction pathway. However, there is no direct evidence for the participation of this radical pair. The intermediate could be depicted as the thermally equilibrated LTMCT excited state of the six-coordinate starting material or as a monodentate DTC with one uncoordinated sulfur with equal validity. In an attempt to directly observe the free radical ligand, the photoreaction was carried out in a probe of an ESR spectrometer. No organic free radical was observed in the region of $g = 2$. The absence of a signal could arise because of a short lifetime of the radical pair and the concomitant low steady state concentration. Alternatively, magnetic exchange between the free radical and the metal could also be responsible for the absence of a signal in this region. Thus, the ESR results are inconclusive. The alternatives presented above represent conceptual extremes which, in all cases, lead to the photoproduction of the five-coordinate iron(III) complex via homolytic iron-sulfur bond cleavage.

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References and Notes

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Spectral Properties of Organometallic Transition Metal Complexes. 2. The Solution Structure of Sodium Dicarbonyl(η^5-cyclopentadienyl)ferrate Involving Direct Sodium-Iron Ion Pairing

K. H. Pannell* and David Jackson

Contribution from the Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968.
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Abstract: The solution spectra of $Na^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ has been recorded in ethereal solvents in the presence of varying amounts of dibenzo-18-crown-6. The resulting spectra indicate the presence of three distinct ion pairs, one of which involves a direct sodium-iron interaction, another a more normal sodium-carbonyl oxygen interaction, and a third solvent separated ion pair. The related molybdenum anion, $Na^+[(\eta^5\text{-}C_5H_5)Mo(CO)_2P(OPh)_3]^-$, exhibits only two ion pairs, a sodium-carbonyl oxygen bonded tight ion pair and the solvent separated ion pair.

There has recently been considerable interest in the solution structure of the alkali metal salts of various transition metal carbonylate anions. Extensive studies by Edgell and co-workers on the sodium tetracarbonylcobaltate were the first to illustrate the importance of ion pairing in such systems.[1-3] It was shown that an equilibrium existed between a tight ion pair involving a sodium-carbonyl oxygen interaction and a solvent separated ion pair.

$$Co^-(CO)_3C{\equiv}ONa^+S \rightleftharpoons Co^-(CO)_4 + SNa^+$$

Later studies by Pribula and Brown reported similar ion pairs existed for the sodium pentacarbonylmanganate system,[4] while Collman et al. have reported that the chemical reactivity of $Fe(CO)_4{}^{2-}2Na^+$ with alkyl halides is very dependent upon