the exception of the edge-displacement model, other models of ligand field photolysis treat photoinduced isomerization as a secondary, and unexplained, phenomenon which occurs after the primary step of ligand aquation. Stereochemical rearrangements are common to the ligand field photochemistry of Co(III), Rh(III), and even Cr(III),[24] and several studies[15,25] have now shown that the bonding configuration of innocent, nonlabilized ligands can affect the course of a photoinduced reaction. The clear implication is that photochemical models must be developed which deal with the distortion of the entire complex in the excited state rather than merely the radial distortion of a single ligand. Work is currently in progress to test the validity of the TBP model in the photochemical behavior of other d^6 complexes.

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Registry No. *cis*-α-[Rh(trien)Cl_2]$^+$, 67951-70-6; *cis*-α-[Rh(trien)Cl(H_2O)]$^{2+}$, 67951-71-7; *cis*-β-[Rh(trien)Cl_2]$^+$, 67951-72-8; *cis*-β-[Rh(trien)Cl(H_2O)]$^{2+}$, 68035-69-8; *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$, 67999-49-9.

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(10) Abbreviations used throughout: cyclam = 1,4,8,11-tetraazacyclotetradecane, trien = 1,4,7,10-tetraazadecane, tren = β,β',β''-triaminotriethylamine.

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(26) An apparent anomaly has been reported,[9] as ligand field excitation of complexes of the form *cis*-[Rh(cyclam)X_2]$^+$ (X = Cl, Br, I) "proceed by halide aquation with complete isomeric retention in the hydrolyzed product". These photolyses were done at "natural pH" in 90%/10% H_2O–CH_3CN solutions, no limits were set on the amount of *trans* product which would have gone undetected, and the extent of photolysis was not reported, so it is not clear whether comparison to the *cis*-[Rh(trien)Cl_2]$^+$ studies is appropriate. Assuming such comparisons are valid, the lack of photoinduced aquation/isomerization of *cis*-[Rh(cyclam)X_2]$^+$ is not inconsistent with the reaction model invoked for the less chelated amines. Work with molecular models shows that for *cis*-[Rh(cyclam)X_2]$^+$, and even for [Rh(cyclam)X]$^{2+}$ in a trigonal-bipyramid geometry, the region trans to the coordinated halide(s) is quite hydrophobic due to the methylene groups of the aliphatic cyclam chelate. Nucleophilic water attack in this region, necessary for formation of trans product, could not readily occur, so less hindered cis attack may lead to the observed *cis*-aquochloro ion.

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Photochemistry of Dithiocarbamato Complexes. 2.[1] Photolysis of Iron(III) and Iron(IV) Complexes

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The photochemistry of $Fe(S_2CNR_2)_3$, $[Fe(S_2CNR_2)_3]BF_4$, and $Fe(S_2CNR_2)_2[S_2C_2(CF_3)_2]$ (R = alkyl) in chlorocarbon solvents has been studied. Quantum yield determinations, quantitative organic product analyses, and spectroscopic analyses have led to mechanistic conclusions. $Fe(S_2CNR_2)_3$ is activated by a combination of charge-transfer-to-metal (CTTM) and charge-transfer-to-solvent (CTTS) absorptions, and reaction with RCl to give $Fe(S_2CNR_2)_2Cl$ is thought to occur via electron transfer to RCl from CT-activated $Fe(S_2CNR_2)_3$. CTTS excitation gives this electron transfer directly. The resulting species $Fe(S_2CNR_2)_3^+$ and Cl^- react giving the observed products. Chemical evidence for this reaction sequence will be presented. The CT photoreactivity of $Fe(S_2CNR_2)_3^+$ is thought to occur by dissociation of $S_2CNR_2^+$ from the excited state with subsequent reaction of $Fe(S_2CNR_2)_2$ with RCl giving $Fe(S_2CNR_2)_2Cl$. The CT excited state of $Fe(S_2CNR_2)_2[S_2C_2(CF_3)_2]$ dissociates the neutral dithietene molecule. Photochemical studies of NaS_2CNR_2, the disulfide $(S_2CNR_2)_2$, and the phenyl ester $PhSC(S)NR_2$ have also been carried out in order to verify the reaction sequences of the metal complexes.

Introduction

The charge-transfer photochemistry of transition-metal complexes with sulfur-containing ligands has proved to be an area of increasing interest.[1,3-8] The first reaction studied using metal complexes of the dithiocarbamate ligand (*N*,*N*-dialkyldithiocarbamate = $S_2CNR_2^- = R_2dtc^-$) was the reversible photobleaching of tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide, $[Ni(Bu_2dtc)_3]Br$, in acetonitrile solution given by eq 1.[3,6] $(Bu_2dtc)_2$ is tetra-*n*-butylthiuram disulfide.

$$\mathrm{Ni(Bu_2dtc)_3^+ + Br^- \underset{dark}{\overset{h\nu}{\rightleftharpoons}} {}^1/_2Ni(Bu_2dtc)_2 + {}^1/_2NiBr_2 + (Bu_2dtc)_2} \qquad (1)$$

A previous communication from our laboratory showed that tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complexes, $Fe(R_2dtc)_3$, react photochemically with chlorocarbon organic

Table I. Disappearance Quantum Yields for the Photolysis of Iron Dithiocarbamate Complexes in Chlorine-Containing Solvents[a]

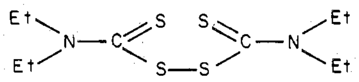
Fe complex	solvent	ϕ(366 nm)	ϕ(313 nm)	ϕ(265 nm)
$Fe(Et_2dtc)_3$	C_6H_5Cl	0.011	0.070	0.39
	2% C_6H_5Cl/ 98% CH_3CN[b]			0.092
	$CHCl_3$	0.050	0.15	0.26
	2% $CHCl_3$/ 98% CH_3CN[b]			0.032
	n-C_4H_9Cl	0.01	0.02	0.04
	CH_3CN			0.003[c]
$Fe(pyrrdtc)_3$	$CHCl_3$	0.019	0.059	0.18
$Fe(Oct_2dtc)_3$	$CHCl_3$			0.17
$[Fe(Et_2dtc)_3]BF_4$	$CHCl_3$	0.002	0.021	0.060
$Fe(Et_2dtc)_2(tfd)$	$CHCl_3$	0.003	0.025	0.12
$Fe(Et_2dtc)_2Cl$	$CHCl_3$	<0.001	<0.001	0.017

[a] All quantum yields were measured under an inert atmosphere at 30 °C. Quantum yields are precise to within 10%. [b] Percent by volume. [c] Photodecomposition.

compounds such as chloroform, methylene chloride, and chlorobenzene to yield the five-coordinate iron(III) complexes $Fe(R_2dtc)_2Cl$ according to eq 2.[1] Additional aspects of this

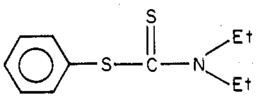
$$Fe(R_2dtc)_3 + RCl \xrightarrow{h\nu} Fe(R_2dtc)_2Cl + \text{organic byproducts} \quad (2)$$

reaction have been reported by Zink and co-workers.[7,8] In this paper we report in detail further studies into the mechanism of the photochemical reactions of iron(III) and -(IV) tris(dithiocarbamate) complexes with chlorocarbon solvents. In addition, we describe some of the photochemistry of the following compounds: $Fe(Et_2dtc)_2[S_2C_2(CF_3)_2]$, $[Fe(Et_2dtc)_3]BF_4$, the dithiocarbamate anion (Et_2dtc^-), and tetraethylthiuram disulfide (Et_4tds), I.



I

In previous studies on reaction 2 it has been important to isolate and identify all organic and inorganic products of photolysis. We have previously shown that irradiation of $Fe(Et_2dtc)_3$ in chlorobenzene yields primarily the thioester II



II

as well as other minor organic products.[1] This thioester has also been observed in the photochemical reaction of $Ru(R_2dtc)_3$ with chlorobenzene.[4,9] In this paper we describe the photochemistry of the thioester II and discuss its significance as a product in the reactions mentioned above.

The photochemical reaction of $Fe(R_2dtc)_3$ with chlorocarbon organic compounds, eq 2, results upon irradiation of the intense charge-transfer bands at 265 nm. We previously described the photoactive excited state to be of the charge-transfer-to-metal (CTTM) type;[1] however, experiments described in this paper suggest that charge-transfer-to-solvent (CTTS) excitations may in fact be partly responsible for the observed reaction at 265 nm.

Results and Discussion

Representative quantum yields for the photolysis of iron dithiocarbamate complexes in chlorocarbon solvents are given in Table I. The quantum yields reported are for the disappearance of the starting complexes (see Experimental Section).

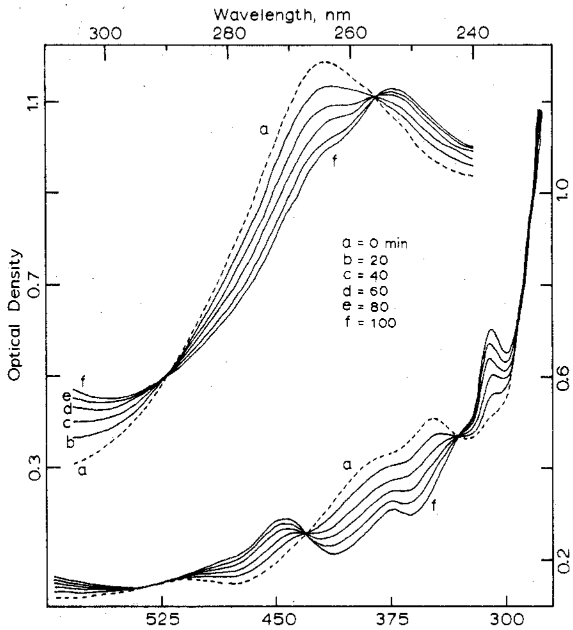
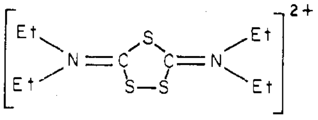


Figure 1. Spectral changes during photolysis at 265 nm of 4.03 × 10^{-5} M $Fe(Et_2dtc)_3$ in $CHCl_3$ solution at 30 °C in the 600–300-nm region. The 300–240-nm spectral changes are shown for photolysis of 2.35 × 10^{-5} M $Fe(Et_2dtc)_3$ under the same conditions.

Chlorine Abstraction by $Fe(Et_2dtc)_3$. Photolysis (265 nm) of the brown $Fe(R_2dtc)_3$ complexes in the presence of chlorocarbon organic compounds R′Cl (R = alkyl, aryl) results in the formation of green $Fe(R_2dtc)_2Cl$. These five-coordinate complexes are known[10] and were identified by UV-vis, IR, and ^1H NMR spectroscopy of isolated samples.[1] This reaction is general for a large number of dithiocarbamates, including R = ethyl, isopropyl, n-butyl, n-octyl, pyrrolidyl, and benzyl, and occurs using a wide variety of chlorine-containing organic compounds, including chloroform, methylene chloride, carbon tetrachloride, chlorobenzene, o- and p-chlorobiphenyl, and bornyl chloride.

Electronic spectra obtained during 265-nm irradiation of $Fe(Et_2dtc)_3$ in chloroform exhibit five isosbestic points, as shown in Figure 1.[11] These isosbestic points persist until the reaction has gone nearly to completion, when photolysis of the primary metal-containing product, $Fe(Et_2dtc)_2Cl$, becomes significant, although at a much slower rate (see Table I). The spectra displayed in Figure 1 show the spectral changes which occur when $Fe(Et_2dtc)_3$ almost completely changes into $Fe(Et_2dtc)_2Cl$ (only a spectrophotometrically undetectable amount of $Fe(Et_2dtc)_3$ remains after 100 min of photolysis). Further evidence for a stoichiometric reaction is provided by carefully monitoring the progress of the reaction. Disappearance and appearance quantum yields were determined by monitoring spectral changes at 350 and 480 nm, where $Fe(Et_2dtc)_3$ and $Fe(Et_2dtc)_2Cl$ predominantly absorb, respectively. Simultaneous equations were solved for concentrations using independently determined extinction coefficients for $Fe(Et_2dtc)_3$ and $Fe(Et_2dtc)_2Cl$. The appearance and disappearance quantum yields for the reaction in $CHCl_3$ and C_6H_5Cl, respectively, are identical within experimental error. Exhaustive photolysis eventually results in a yellow solution having absorption maxima at 364 and 318 nm. This spectrum is identical with that reported for $FeCl_4^-$,[12] and it is the same as that obtained when excess HCl is bubbled through a solution of $Fe(Et_2dtc)_3$ in $CHCl_3$. The counterion present along with $FeCl_4^-$ is compound III.[13] This dication was identified by its



III

^{1}H NMR and IR spectra.[13] The photolysis of $Fe(Et_2dtc)_2Cl$ was not studied in detail.

In all cases, the quantum yields increased with decreasing wavelength or with increasing energy. The Hg-vapor lines of wavelength higher than 366 nm are not of sufficient energy to cause an observable reaction. In no cases do parallel thermal reactions occur. In fact, $Fe(Et_2dtc)_3$ can be refluxed overnight in chloroform or chlorobenzene in the dark without the formation of detectable amounts of $Fe(Et_2dtc)_2Cl$.

The only solvent which absorbs appreciable amounts of light at the wavelengths studied is chlorobenzene. It is important to note that chlorobenzene reacts more slowly than chloroform at all wavelengths except 265 nm, where chlorobenzene absorbs a significant amount of light. It can therefore be concluded that direct photolysis of solvent also initiates the reaction, probably by the production of chlorine radicals.[14] However, solvent photolysis leads to the formation of undesirable organic byproducts (vide infra). It is possible to minimize C_6H_5Cl photolysis by dilution in a nonreactive solvent such as acetonitrile (vide infra). When this is done, the quantum yield decreases, as shown in Table I. See ref 8 for a detailed discussion of the effects of dilution in inert solvents. Solvent photolysis is not responsible for the reaction in $CHCl_3$ or dilute C_6H_5Cl because $CHCl_3$ does not absorb at wavelengths where the reaction occurs ($\lambda \geq 265$ nm) and the organic products are not those expected for C_6H_5Cl irradiation (vida infra).[15]

The secondary photochemical reaction of $Fe(Et_2dtc)_2Cl$ occurs much more slowly than the primary photoreaction, as shown by the quantum yields in Table I. $Fe(Et_2dtc)_2Cl$ has strong UV bands at 310 and 260 nm. The 260-nm band appears to be the only one to show detectable photoactivity. Although the assignment of the electronic absorption spectrum of $Fe(R_2dtc)_2Cl$ has not been made, the bands at 310 and 260 nm most likely consist of charge-transfer and intraligand transitions.

For insight into the mechanism of the reaction, the organic byproducts of the photolysis of $Fe(Et_2dtc)_3$ in chlorobenzene were examined. These byproducts were identified by IR, GLC, and mass spectral data, including GC/MS analysis. All photolysis experiments from which organic products were isolated were performed by diluting the chlorobenzene in acetonitrile, a nonreactive solvent (Table I), and adjusting the concentration of $Fe(Et_2dtc)_3$ so that >95% of the light was absorbed by the complex and <5% by the chlorobenzene (see Experimental Section). This procedure was necessary to minimize direct photolysis of the chlorobenzene.[16] These experiments were carried out using light of 265 nm and higher wavelengths. The major organic byproducts found are the thioester II and phenyl disulfide, IV, although trace amounts of other compounds are also observed (see Chart I).

Chart I

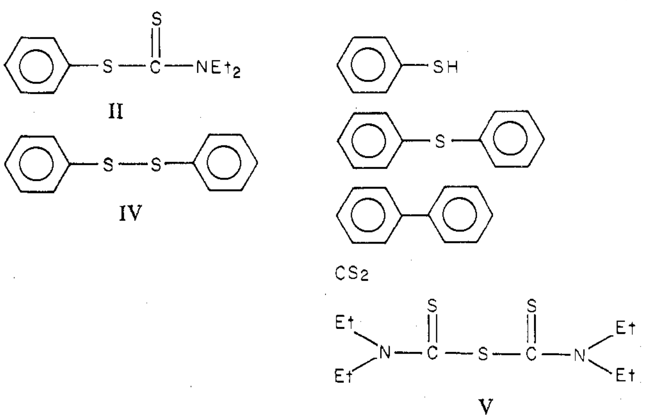


Table II. Organic Products for the Photochemical Reaction of $Fe(Et_2dtc)_3$ with C_6H_5Cl[a]

% $Fe(Et_2dtc)_3$ reacted[b]	% yield		
	C_6H_5-SC(S)NEt_2	C_6H_5-SSC_6H_5	total[c]
7.2	83.8	7.9	99.6
10.1	53.7	16.0	85.7
14.2	33.0	19.6	72.2
18.6	23.1	16.3	55.7

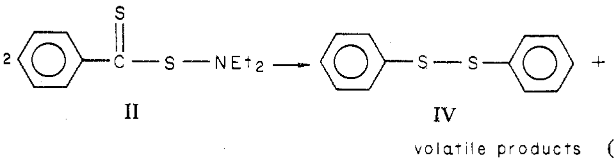
[a] All yields are based on the amount of $Fe(Et_2dtc)_3$ reacted. Products measured by GLC integration. See Experimental Section for details. [b] Initial $[Fe(Et_2dtc)_3] = 2.91 \times 10^{-3}$ M. [c] Total % yield = % yield of $C_6H_5SC(S)NEt_2$ + 2 × % yield of $C_6H_5SSC_6H_5$, since 1 mol of phenyl disulfide is formed from photolysis of *2 mol* of the thioester (see text).

Table III. Data for Photolysis of $C_6H_5SC(S)NEt_2$ in *n*-Pentane

time, min	% C_6H_5-SC(S)NEt_2 remaining[a] (*A*)	% yield of C_6H_5-SSC_6H_5[a] (*B*)	*A* + 2*B*[b,c]
0	100	0	100
80	71.8	9.7	91.2
160	48.5	14.5	77.5
240	34.4	18.5	71.4
360	20.3	21.2	62.6
480	15.0	18.9	52.9

[a] Based on initial concentration of $C_6H_5SC(S)NEt_2$. [b] Measures total amount of C_6H_5S present in solution (see text). [c] Small amounts of thiophenol were also observed.

When samples were taken during the photolysis of $Fe(Et_2dtc)_3$ in chlorobenzene and analyzed by gas chromatography for organic byproducts, it was found that initially the chief organic product was the thioester $C_6H_5SC(S)NEt_2$, II. As the reaction progressed, the proportion of thioester decreased, while that of phenyl disulfide, $C_6H_5SSC_6H_5$, IV, steadily increased. The results of this experiment are given in Table II. Eventually the amount of phenyl disulfide also began to decrease. It should be noted that, if phenyl disulfide, IV, was formed by secondary photolysis of the thioester II, it would be necessary to photolyze *2 mol* of thioester to obtain 1 mol of phenyl disulfide according to eq 3. This reaction does indeed occur as evidenced by photolysis experiments using II (vide infra).



(3)

The thioester II has been reported to yield $C_6H_5S\cdot$ radicals when used to accelerate the polymerization of methylacrylate and styrene.[17] Our experiments verify that the C_6H_5S–C bond is the one preferentially ruptured when II is photolyzed. Photolysis of II in pentane at 265 nm yielded phenyl disulfide, IV, as the main product (see Table III). The disappearance quantum yield for II is 0.5 at 265 nm. These results are very similar to those obtained for the photolysis of $Fe(Et_2dtc)_3$ in chlorobenzene, as a comparison of Tables II and III shows. In both cases, the thioester photolyzes to give phenyl disulfide, which increases in concentration until it too begins to photo decompose. As both II and IV photolyze, several compounds including the minor byproducts listed in Chart I are formed. Traces of tetraethylthiuram disulfide, I, can also be detected by NMR and mass spectrometry.[18]

The results presented above for the irradiation of $\mathrm{Fe(Et_2dtc)_3}$ at $\lambda > 265$ nm in chlorobenzene diluted with acetonitrile clearly show that the phenyl ester II is initially formed in nearly quantitative yield. Indeed, after conversion of 7.2 mol % of $\mathrm{Fe(Et_2dtc)_3}$ into $\mathrm{Fe(Et_2dtc)_2Cl}$, 84 mol % of the stoichiometric amount (eq 4) of II is observed.

$$\mathrm{Fe(Et_2dtc)_3 + C_6H_5Cl \xrightarrow{h\nu} Fe(Et_2dtc)_2Cl + \underset{II}{C_6H_5SC(S)N(Et)_2}} \tag{4}$$

The 16 mol % of II not observed is completely accounted for by secondary photolysis to phenyl disulfide, IV, according to eq 3 (see Table II). Therefore eq 4 summarizes the primary photochemical reaction with chlorobenzene. During continued irradiation at 265 nm the major organic products II and IV are decomposed into volatile unidentified compounds and the minor products discussed above. The decreasing total percent yield of II + 2(IV) shown in Table II results from this decomposition.

Thioester products such as II are not observed upon photolysis of $\mathrm{Fe(Et_2dtc)_3}$ in $\mathrm{CHCl_3}$ or $\mathrm{CH_2Cl_2}$. The products expected here by analogy to eq 4 would not be stable under the conditions of the reaction, and the only identified compounds are small amounts of thiuram disulfide I and thiuram monosulfide V. These products most likely result from secondary photolysis or decomposition, and their photochemical formation will be discussed in a later section. It is important that no diesters are produced in the $\mathrm{CH_2Cl_2}$ reaction since it is known that $\mathrm{CH_2Cl_2}$ and $\mathrm{NaEt_2dtc}$ react thermally to give the diester $\mathrm{Et_2NC(S)SCH_2SC(S)NEt_2}$.[19] This result argues against the possibility of $\mathrm{Et_2dtc^-}$ photodissociation. Indeed, in all of our photochemical studies with dithiocarbamato complexes there has not been any evidence for ligand anion dissociation.[1,4,5]

Photolysis of $\mathrm{Fe(R_2dtc)_3}$ with chlorobenzene or $\mathrm{CHCl_3}$ using irradiating wavelengths of 313 and 366 nm results in the same metal-containing product observed with 265-nm irradiation. The reaction is stoichiometric in metal in all cases as determined by spectroscopic monitoring (isosbestic points as in Figure 1) and product isolation. The quantum yields are significantly smaller, however, for the higher wavelength irradiations. Although organic products for the chlorobenzene reaction were not determined for photolysis at 313 or 366 nm, it is likely that II is formed as shown in eq 4.

Mechanism of Chlorine Abstraction. In a preliminary communication of this work we postulated a mechanistic scheme which involved a CTTM excited state, $\mathrm{[Fe(dtc)_2{-}{-}{-}dtc\cdot]^*}$, which underwent chlorine radical abstraction from RCl.[1] This was based in part on Nikolov's[20] spectral assignments for $\mathrm{Fe(Et_2dtc)_3}$ and on the fact that bis- and tris(dithiocarbamato)iron(II) complexes react with $\mathrm{CHCl_3}$ in the dark producing $\mathrm{Fe(dtc)_2Cl}$.[1] Since our initial communication, a new and more detailed spectral assignment has been made by Manoussakis[21] and continued work in our laboratory on this and related photochemical reactions has led to a more detailed mechanism. First the mechanism will be described and then it will be justified. Equations 5–9 represent a mechanistic scheme which is consistent with the experimental results outlined below (dtc = $\mathrm{Et_2dtc}$).

$$\mathrm{Fe(dtc)_3 \xrightarrow[265\text{–}366\ nm]{h\nu} [Fe(dtc)_3]_{CT}^*} \tag{5}$$

$$\mathrm{[Fe(dtc)_3]_{CT}^* + RCl \rightarrow [Fe(dtc)_3^+{-}{-}{-}RCl^{-}\cdot]} \tag{6}$$

$$\mathrm{[Fe(dtc)_3{-}{-}{-}RCl] \xrightarrow[\lambda < 300\ nm]{h\nu} [Fe(dtc)_3^+{-}{-}{-}RCl^{-}\cdot]} \tag{7}$$

$$\mathrm{[Fe(dtc)_3^+{-}{-}{-}RCl^{-}\cdot] \rightarrow [Fe(dtc)_2Cl{-}{-}{-}dtc\cdot{-}{-}{-}R\cdot]} \tag{8}$$

$$\mathrm{[Fe(dtc)_2Cl{-}{-}{-}dtc\cdot{-}{-}{-}R\cdot] \rightarrow Fe(dtc)_2Cl + \underset{II}{dtcR}} \tag{9}$$

The initial absorption of radiation between 265 and 366 nm leads to a charge-transfer excited state (eq 5) which is quenched by chloroform or chlorobenzene via electron transfer, forming the radical pair $\mathrm{[Fe(dtc)_3^+{-}{-}{-}RCl^{-}\cdot]}$ (eq 6). This radical pair can alternatively be formed by direct charge-transfer-to-solvent (CTTS) excitation (eq 7). The absorption spectra reveal a band in the 270–280-nm region which is consistent with a CTTS excitation (vide infra).[22,23] However, photolysis at wavelengths greater than 300 nm cannot excite the CTTS band since its extinction coefficient becomes zero in this region. The formation of the CT excited state (eq 5) most likely results from either CTTM ($\pi \rightarrow e_g^*$) or intraligand ($\pi \rightarrow \pi^*$) excitation since bands assignable to both transitions are present in the 265–366-nm region (vide infra).[21] However, the intraligand bands only occur in the spectral region below 300 nm.[21,24] We suggest that the $\mathrm{RCl^{-}\cdot}$ radical anion transfers a chloride ion to $\mathrm{Fe(dtc)_3^+}$ which releases a dtc· radical (eq 8). The dtc· radical is then scavenged by R· within the solvent cage since when R = phenyl the ester II is formed quantitatively.

Chemical and spectroscopic evidence for the above mechanistic scheme is outlined below in more detail.

(a) Spectral Assignments and the CT Nature of the Excited State. The UV–vis spectrum of $\mathrm{Fe(Et_2dtc)_3}$ is shown by line a of Figure 1. The intense bands centered at approximately 350 and 265 nm have been assigned to CTTM ($\pi \rightarrow e_g^*$) and intraligand $\pi \rightarrow \pi^*$ transitions,[21] although another study attributes bands in the 350–265-nm region to a combination of CTTM and CTTL absorptions.[20] Due to the complexity of assigning the spectral bands in a spin crossover system such as exists in $\mathrm{Fe(Et_2dtc)_3}$ (d^5, $S = {}^1/_2 \rightleftharpoons S = {}^5/_2$),[25] it is certain only that the intense bands in the spectral region of interest correspond to CT and, for $\lambda < 300$ nm, intraligand transitions. In either case CT excited states are likely and consistent with the observed photoreactivity.

The CT excited complex, $\mathrm{[Fe(dtc)_3]_{CT}^*}$, in eq 5 should be a better reductant and oxidant than in its ground state. The excited state results from absorption of radiation with $\lambda \lesssim 366$ nm which corresponds to an energy $\gtrsim 3.4$ eV. Recent work by Meyer[26] on charge-transfer excited states suggests that nearly all of the excitation energy can be used to increase both the oxidation and reduction potentials of the excited state relative to the ground state. In this case the electron transfer from $\mathrm{[Fe(dtc)_3]_{CT}^*}$ to the chloroform is a thermodynamically favored process[27] and very similar to the initial electron transfer to $\mathrm{CHCl_3}$ from the CT excited state of hexakis(arylisocyano) complexes of tungsten and molybdenum recently reported.[30]

(b) CTTS Excitation. Since the radical pair $\mathrm{[Fe(dtc)_3^+{-}{-}{-}RCl^{-}\cdot]}$ can also result from CTTS excitation (eq 7) and since several recent reports strongly implicate this process in chlorinated solvents,[22,23] a careful examination of the halocarbon dependence of the UV spectra was undertaken. Although the main features of the near-UV spectra of $\mathrm{Fe(Et_2dtc)_3}$ are independent of the solvent ($\mathrm{CH_3CN}$, $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$, $\mathrm{CCl_4}$), small but important differences were observed. In carefully recorded difference spectra of $\mathrm{Fe(Et_2dtc)_3}$ between $\mathrm{CH_3CN}$ and the chlorocarbons listed above (see Figure 2), absorption bands appeared in the 270–280-nm region which are best attributed to CTTS transitions. The CTTS assignment follows from the correlation of CTTS maxima to the ease of reduction of the chlorocarbon, Table IV. The more easily reduced chlorocarbons exhibit the lower energy CTTS maxima. In addition, the magnitude of the shifts and intensities of the CTTS bands are quite similar to those observed

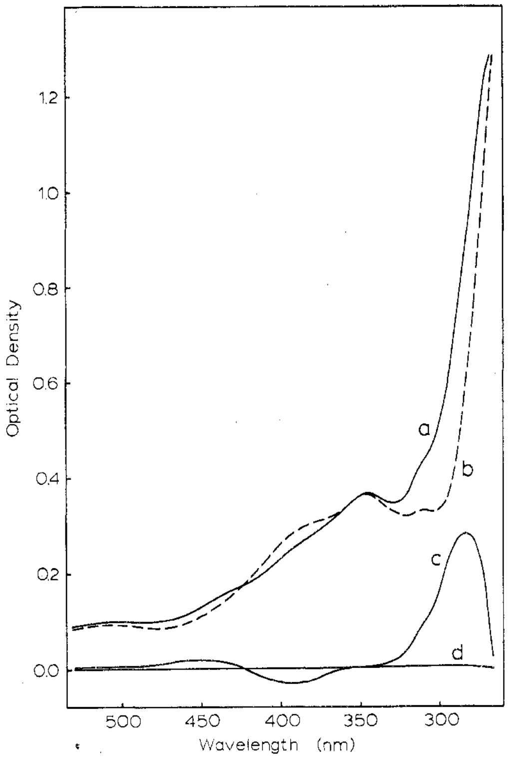


Figure 2. Optical spectral of 3.00×10^{-5} M $Fe(Et_2dtc)_3$ in CCl_4 at 30 °C, curve a, and in CH_3CN, curve b, and the difference spectrum between a and b, curve c. Curve d is the baseline.

Table IV. Difference Spectral Data for $Fe(Et_2dtc)_3$

sample compartment[a]	λ,[b] nm	$\Delta\epsilon$[c]	$E_{1/2}$ of solvent,[d] V vs. SCE
CH_2Cl_2	273	2800	−2.33
$CHCl_3$	280	3900	−1.67
CCl_4	283	10000	−0.78

[a] 1.00×10^{-4} M in solvent indicated; CH_3CN in reference compartment. [b] Maximum λ of CTTS transition. [c] Change in molar absorptivity associated with CTTS. [d] Reduction potential of solvent ($E_{1/2}$ values from C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970).

with ferrocene[22] and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$[23] in the same solvents. The quantum efficiency for chlorine abstraction is maximum at 265 nm (Table I), which could be due to excitation via CTTS (eq 7) in addition to CT and intraligand excitation (eq 5). CTTS excitation cannot be important for irradiation at λ >300 nm and in this region the quantum efficiency is much smaller. A CTTS transition has also been observed with $Ru(Et_2dtc)_3$ and $Os(Et_2dtc)_3$ in chlorocarbon solvents, and excitation via this mechanism is probably partly responsible for the photochemical chlorine abstraction to $Ru(Et_2dtc)_3Cl$[4,5,9] and $Os(Et_2dtc)_3Cl$.[31]

(c) Chemical Evidence for the Mechanism. The radical pair $[Fe(dtc)_3{}^+\text{---}RCl^{-}\cdot]$ could collapse in a number of ways but the process shown by eq 8 and 9 is most consistent with the chemical data. For example, if the chlorocarbon radical anion were to escape the solvent cage, the expected products would be $[Fe(dtc)_3]^+$, Cl^-, and R·. The R· radical would react with solvent, and for R = phenyl the expected products would be chlorinated biphenyls and biphenyl. None of these organic products are observed and since Ph(dtc) II is quantitatively formed, it is concluded that $PhCl^{-}\cdot$ does not escape the solvent cage. The reaction of Cl^- with $[Fe(Et_2dtc)_3]BF_4$[32] was carried out in $CHCl_3$ solvent in the dark in order to test eq 8 in which Cl^- is transferred to $[Fe(dtc)_3]^+$ within the solvent cage. The reaction produced $Fe(Et_2dtc)_2Cl$ and thiuram disulfide I quantitatively, demonstrating the likeliness of eq 8. It is important to note, however, that photolysis of $Fe(Et_2dtc)_3$ in CH_3CN in the presence of free Cl^- does not result in the formation of $Fe(Et_2dtc)_2Cl$.[1,7] Therefore, Cl^- will only produce the observed photoproduct if $Fe(Et_2dtc)_3{}^+$ is present.

Equation 9 follows since dtc· and R· would combine within the solvent cage to form Rdtc II. Additional support for these steps is the absence of thiuram disulfide I formation during the photolysis reaction. If dtc· radicals escaped the solvent cage, they would combine forming thiuram disulfide I.[33] The photolysis of I in chlorobenzene yields only trace amounts of II (vide infra) and we have shown that dtc· radicals do not react with chlorobenzene thermally.[34] Therefore the quantitative formation of the phenyl ester II provides support for the reactions shown in eq 8 and 9 and eliminates the possibility of dtc· free-radical dissociation.

As mentioned above, it is also possible that in place of the reactions shown in eq 8 and 9, the radical anion $RCl^{-}\cdot$ could transfer a chlorine radical to $Fe(dtc)_3{}^+$, producing $Fe(dtc)_2Cl$, dtc^+, and R^- which would lead to the observed products. Evidence for dtc^+ photodissociation from $[Fe(dtc)_3]BF_4$ will be presented later. Since $Fe(dtc)_3$ can be converted into $Fe(dtc)_2Cl$ by free-radical initiators in $CHCl_3$,[7] the chlorine radical transfer step cannot be precluded. Since $RCl^{-}\cdot$ radical ions are known to dissociate into R· and Cl^-,[29] the mechanism shown in eq 8 and 9 is favored. Additionally, it is likely that conversion of $Fe(dtc)_3$ into $Fe(dtc)_2Cl$ via free-radical initiators in $CHCl_3$ or by reaction with anhydrous HCl in the dark occurs by a different mechanism.

The mechanism originally proposed by Zink[7] and by us[1] for the photochemical chlorine abstraction by $Fe(dtc)_3$ involved the following steps: (i) photoreduction to $[Fe(dtc)_2\text{---}dtc\cdot]^*$ via CTTM excitation, (ii) chlorine radical abstraction from RCl, and (iii) combination of dtc· and R· giving the observed ester II. The best support for steps (i) and (ii) of this mechanism is the observation that $Fe(dtc)_2$ reacts rapidly with $CHCl_3$ at 25 °C in the dark to yield $Fe(dtc)_2Cl$.[1] Step (iii) follows because the observed organic product is II when R is phenyl. Although this scheme is possible, we prefer the mechanism summarized by eq 5–9 because there is precedence for electron-transfer quenching of CT excited states[26,30] and there is good evidence for CTTS excitation in this system. Additionally, the observed photochemical reactions of $Ru(Et_2dtc)_3$[4,5] and $Os(Et_2dtc)_3$ with $CHCl_3$ give $Ru(Et_2dtc)_3Cl$ and $Os(Et_2dtc)_3Cl$, respectively, as primary products. It is probable that a similar photochemical mechanism occurs with Fe, Ru, and Os, and since Ru(IV) and Os(IV) products are found, it is likely that chloride transfer to a tetravalent metal oxidation state occurs.

Photochemistry of $[Fe(Et_2dtc)_3]BF_4$. The iron(IV) complex $[Fe(Et_2dtc)_3]BF_4$[32] reacts photochemically with chlorocarbon organic compounds to form $Fe(Et_2dtc)_2Cl$, but with much smaller quantum yields than $Fe(Et_2dtc)_3$, as shown in Table I. During the early portion of the reaction in $CHCl_3$, the electronic absorption spectrum of a photolyzed solution of $[Fe(Et_2dtc)_3]BF_4$ exhibits spectral changes corresponding to direct conversion of $[Fe(Et_2dtc)_3]BF_4$ to $Fe(Et_2dtc)_2Cl$, as shown in Figure 3. Since $Fe(Et_2dtc)_2Cl$ absorbs less light than $[Fe(Et_2dtc)_3]BF_4$ in most regions of the spectrum, only one isosbestic point is observed, at 260 nm. Because of the low quantum yield of this reaction, photolysis of the product, $Fe(Et_2dtc)_2Cl$, becomes significant, and this secondary photolysis is observed before the initial reaction has gone to completion. Therefore the 130-min trace in Figure 3 represents only 72% conversion of $[Fe(Et_2dtc)_3]BF_4$ to $Fe(Et_2dtc)_2Cl$.

During photolysis of $[Fe(Et_2dtc)_3]BF_4$ in $CHCl_3$ or CH_2Cl_2 with λ >272 nm, a yellow solid precipitates. This solid

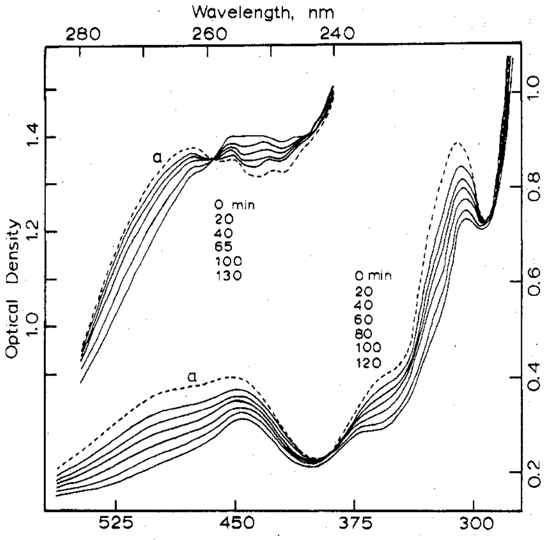


Figure 3. Spectral changes during photolysis at 265 nm of 4.84 × 10^{-5} M $[Fe(Et_2dtc)_3]BF_4$ in $CHCl_3$ solution at 30 °C.

generally forms when the brown color of the Fe(IV) complex changes to green. The yellow solid has ^1H NMR and IR spectra identical with those of the dication III. Small amounts of thiuram disulfide I and monosulfide V are also found. Reactions using chlorobenzene were not studied in detail due to the slowness of the reaction. However, the same metal-containing products are formed quantitatively in chlorobenzene as in $CHCl_3$ and CH_2Cl_2. The formation of dication III suggests the following mechanistic scheme (eq 10–13).

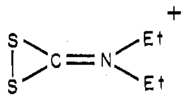
$$[Fe(dtc)_3]^+ \xrightarrow[\text{CTTM}]{h\nu} [Fe(dtc)_2\text{---}dtc^+]^* \qquad (10)$$

$$[Fe(dtc)_2\text{---}dtc^+]^* \rightarrow Fe(dtc)_2 + dtc^+ = {}^1/_2(dtc)_2{}^{2+} \qquad (11)$$

$$Fe(dtc)_2 + RCl \rightarrow Fe(dtc)_2Cl + R\cdot \qquad (12)$$

$${}^1/_2(dtc)_2{}^{2+} \rightarrow {}^1/_2III + S \qquad (13)$$

Although the electronic absorption spectrum of $[Fe(Et_2dtc)_3]^+$ has not been assigned, it is unlikely that CTTL or CTTS transitions occur since the metal is already highly oxidized. Therefore it is likely that excitation occurs via CTTM absorption. We suggest that dtc^+ dissociation occurs for two reasons. First, it has been shown[13] that $[Ru(Et_2dtc)_3]^+$ dissociates Et_2dtc^+ thermally in acetone solution forming $(Et_2dtc)_2{}^{2+}$; and second, the formation of dtc^+ most easily explains the production of III.[13] The existence of dtc^+ has also been discussed by Willemse[35] and the ion probably has structure VI. Dissociation of VI would leave the very reactive complex $Fe(dtc)_2$ which is known to abstract a chlorine radical from $CHCl_3$ in the dark. The eventual production of III from $(dtc)_2{}^{2+}$ is known to occur[13] and III is the ultimate product of the electrochemical 2e⁻ oxidation of tds.[36] The reaction scheme shown by eq 10–13 predicts that Rdtc should not be produced and indeed II is not observed for irradiation in C_6H_5Cl with λ >310 nm.



VI

Photochemistry of $Fe(Et_2dtc)_2[S_2C_2(CF_3)_2]$. $Fe(Et_2dtc)_2$(tfd) also photolyzes in chlorocarbon solvents such as chloroform, methylene chloride, and chlorobenzene to form the five-coordinate complex $Fe(Et_2dtc)_2Cl$. Quantum yields for this reaction in $CHCl_3$ are shown in Table I. During the course of this reaction, four isosbestic points appear in the electronic spectrum, as shown in Figure 4, and they persist until the reaction has gone nearly to completion. As in the case of $Fe(Et_2dtc)_3$, continued photolysis beyond the formation of $Fe(Et_2dtc)_2Cl$ gives a yellow solution with an electronic spectrum matching that reported for $FeCl_4^-$.[12] $Fe(Et_2dtc)_2$(tfd) does not react with $CHCl_3$ when refluxed for 20 h in the dark.

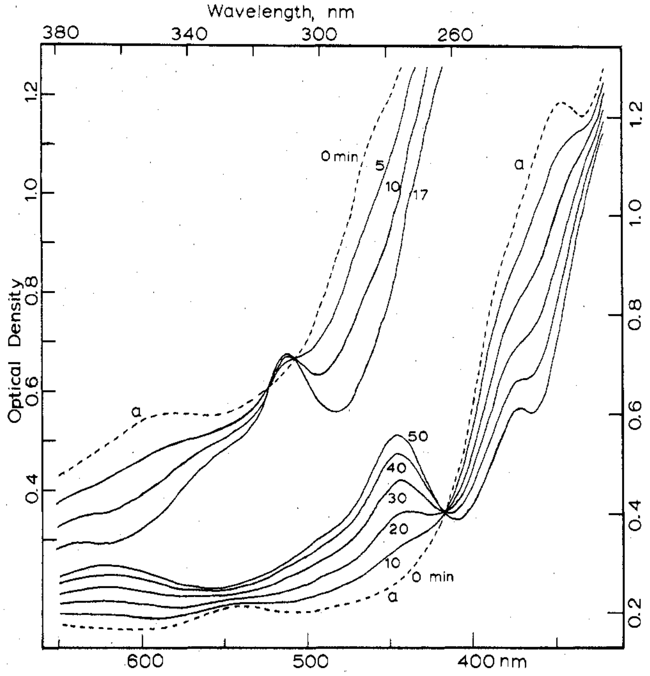


Figure 4. Spectral changes during photolysis at λ >237 nm of 1.35 × 10^{-4} M $Fe(Et_2dtc)_2$(tfd) in $CHCl_3$ solution at 30 °C in the 650–350-nm region. The 380–260-nm spectral changes are shown for photolysis of 6.10 × 10^{-5} M $Fe(Et_2dtc)_2$(tfd) under the same conditions.

Spectral assignments for $Fe(Et_2dtc)_2$(tfd) have not appeared in the literature. However, the electronic spectrum of $Fe(Et_2dtc)_2$(tfd) is very similar to that of $Fe(Et_2dtc)_3$, as can be illustrated by comparing the bands of the two compounds in $CHCl_3$ [λ_{max}, nm (ε, L mol⁻¹ cm⁻¹):

$Fe(Et_2dtc)_2$(tfd)	$Fe(Et_2dtc)_3$
262 (33 800)	265 (47 300)
280 (sh, 27 700)	no distinct band
344 (9080)	350 (11 700)
380 (sh, 6550)	389 (sh, 9300)
541 (1970)	514 (2660)
658 (1700)	590 (1850)
877 (sh, 170)	

From the data in Table I it again appears that the photoactive bands are those farthest into the UV, especially the ones at 262 and/or 280 nm. As for $Fe(Et_2dtc)_3$, these bands are most likely due to CTTM, CTTL, and $\pi \rightarrow \pi^*$ dtc intraligand transitions. The neutral dithietene molecule $S_2C_2(CF_3)_2$ has bands at 238 (ε 7440) and 340 nm (ε 80).[37]

When $Fe(Et_2dtc)_2$(tfd) was photolyzed in neat CH_2Cl_2 at 254 nm,[38] followed by pumping off the solvent at 0 °C, extracting with pentane, and pumping off the pentane at 0 °C, a yellow residue was obtained. The major mass spectral peak with m/e >100 was 226, which corresponds to the mass of the neutral tfd molecule. Other mass spectral fragments matched exactly those obtained independently for a sample of tfd. GLC at 90 °C gave a peak with retention time identical with that of pure tfd. When the iron complex was photolyzed at 254 nm[38] in a solution composed of 2% chlorobenzene and 98% acetonitrile (by volume), there was again mass spectral evi-

Table V. Disappearance Quantum Yields for the Photolysis of Miscellaneous Dithiocarbamate Compounds[a]

compd	solvent	ϕ(265 nm)
$NaEt_2dtc$	10% $CHCl_3$/90% CH_3CN	0.34[b,c]
	CH_3CN	0.17[b,c]
Et_4tds	$CHCl_3$	0.053[b]
$C_6H_5SC(S)NEt_2$	pentane	0.5[d]

[a] All quantum yields were measured under an inert atmosphere at 30 °C. [b] Measured by UV spectral changes. [c] Thermal decomposition subtracted. [d] Measured by GLC integration.

dence for free tfd. No other products were observed in greater than trace amounts with the exception of chlorinated biphenyls. The chlorobenzene was diluted in CH_3CN to minimize the photolysis of the solvent to form chlorobiphenyls and to ensure that >95% of the photons were absorbed by the Fe complex.

The most plausible mechanistic scheme for this reaction is tfd dissociation from a CT excited state and subsequent reaction of $Fe(dtc)_2$ with RCl as shown in eq 12. Although CTTS transitions have not been examined for $Fe(Et_2dtc)_2(tfd)$, their existence is doubtful because the oxidation state of iron is close to +4 and oxidation to a monocation is more difficult than with $Fe(Et_2dtc)_3$ ($E_{1/2}$ vs. SCE: +0.97 and +0.42 V, respectively).[28] Photochemical studies have not been reported on other dithiolene complexes and it should be interesting to compare their excited state reactivities.

Photochemistry of Et_4tds and Et_2dtc^-. Since it is possible that intraligand π–π^* excitation could be contributing to the photochemical processes observed for the metal complexes discussed above, the photolysis of Et_2dtc^- and Et_4tds, I, in the presence of chlorocarbons was studied. Quantum yields for these reactions at 265 nm are presented in Table V.

In experiments with $NaEt_2dtc$, acetonitrile was used as the solvent, and small amounts of chloroform and chlorobenzene were added, with the amount of chlorobenzene restricted so as to absorb <10% of the light at the irradiating wavelengths used. This dilution was made to minimize direct photolysis of the chlorobenzene. Chlorobenzene was always in a molar excess over $NaEt_2dtc$, however (see Experimental Section). $NaEt_2dtc$ was found to decompose rather rapidly on photolysis at 265 nm in CH_3CN at 30 °C as well as in 10% $CHCl_3$/90% CH_3CN, as shown in Table V. In both cases the photodecomposition of $NaEt_2dtc$ was accompanied by a thermal decomposition, making it necessary to subtract the thermal rates to obtain the quantum yields. This thermal reaction has been shown to produce $(Et_2NH_2)(Et_2dtc)$.[39] $NaEt_2dtc$ also was photolyzed in a solution containing 1.7% chlorobenzene and 98.3% CH_3CN by volume at λ >272 nm. During initial stages of the reaction (<4% decomposition), approximately 18% of the dithiocarbamate anion which decomposed could be accounted for as forming the thioester II, $C_6H_5SC(S)NEt_2$, but this percentage fell off to 3.4% by the time the decomposition was one-third complete. The vast majority of the dithiocarbamate anion which reacted most likely resulted in destruction of the ligand to unidentified products, especially since the electronic bands of the ligand at 300 and 264 nm were eventually completely bleached. The small amount of thioester II which did form on photolysis of $NaEt_2dtc$ in the presence of chlorobenzene disappeared rapidly. This is probably a consequence of the limited internal filtering provided by the dithiocarbamate ion.[40] These experiments indicate that uncoordinated Et_2dtc^- is photochemically unstable with respect to decomposition in CH_3CN and chlorocarbon solvents. It is difficult to determine how much ester II is actually formed as a primary product upon photolysis in the presence of chlorobenzene since the secondary photodecomposition of II occurs readily.

Nikolov[24] has assigned the electronic transitions of $NaEt_2dtc$ which occur at 289 and 257 nm in H_2O (300 and 264 nm in acetonitrile) to $\pi \rightarrow \pi^*$ absorptions. It would not be surprising, therefore, if excitation of electrons into π^* orbitals would lead to decomposition of the ligand.

Tetraethylthiuram disulfide, I, undergoes slow photodecomposition in chlorocarbon organic solvents such as chloroform and chlorobenzene. If the solvent consists of 2% chlorobenzene and 98% acetonitrile by volume and photolysis is for λ >272 nm, only 3% of the product can be attributed to the initial formation of II. Thermally, neither II nor phenyl disulfide, IV, is formed. In chloroform, the quantum yield for disappearance of Et_4tds is only 0.053 at 265 nm. A small amount of tetraethylthiuram monosulfide, V, is formed in this reaction, but most of the decomposition products are highly volatile and were not identified. The slow photodecomposition rate of Et_4tds indicates that if it were formed as a product of the 265-nm photolysis of the iron complexes discussed above, it would be easily observed as a reaction product. The fact that Et_4tds, I, is not observed in these reactions (vide supra) and the fact that dtc· free radicals are known to combine into tds in the solvents used provide good evidence that dtc· free radicals are not produced during photolysis of $Fe(dtc)_3$, $[Fe(dtc)_3]^+$, or $Fe(dtc)_2tfd$.

Experimental Section

Preparation of Compounds. $Fe(Et_2dtc)_3$, $Fe(pyrrdtc)_3$,[32b] $ClFe(Et_2dtc)_2$,[10] $[Fe(Et_2dtc)_3]BF_4$,[32a] $Fe(Et_2dtc)_2$,[41] Et_4tds,[42] $NaEt_2dtc$,[43] $III(BF_4)_2$,[13] and $Fe(Et_2dtc)_2(tfd)$[44] were synthesized by literature methods. The amount of H_2O present in the crystalline $NaEt_2dtc$ was measured by titration of the sodium salt with I_2. $CHCl_3$ and CH_2Cl_2 were purified by distillation from BaO under nitrogen and passed down a basic alumina column immediately prior to use. C_6H_5Cl was purified by washing reagent grade C_6H_5Cl with H_2SO_4 and $NaHCO_3$ solutions, drying over anhydrous $MgSO_4$, vacuum distilling into molecular sieves, and passing down a basic alumina column just before use. Reagent grade CH_3CN was distilled from P_2O_5 under nitrogen and stored in the dark over molecular sieves. Other solvents used were reagent grade.

$C_6H_5SC(S)N(C_2H_5)_2$, II, was prepared as follows. Aniline (4.65 g, 50 mmol) was dissolved in a solution containing 10 mL of concentrated HCl and 50 mL of H_2O. The solution was cooled by adding 50 g of ice. To this solution was added 3.5 g (50 mmol) of $NaNO_2$, and the solution was allowed to stand for 15 min. $NaEt_2dtc$ (8.6 g, 50 mmol) was dissolved in 200 mL of H_2O, and 75 g of ice was added. The $NaEt_2dtc$ solution was then added to the original solution, yielding a reddish orange solution. Extraction with petroleum ether gave a yellow oil after evaporation of the solvent. Purified samples of the ester containing ca. 4% phenyl disulfide were obtained by collecting the major peak eluted from a GLC column (5% OV-101 on Chromosorb G) at 200 °C. NMR ($CDCl_3$): δ 8.40 (relative intensity = 5), δ 4.91 (4), δ 2.31 (6); IR (neat): 2991, 2947, 1487 ($\mathrm{C}\overset{..}{-}\mathrm{N}$), 1442, 1416, 1327, 1301, 1269, 1207, 1141, 1068, 1009, 980, 918, 829, 746, 711, 687 cm^{-1}.

Instrumentation. Electronic absorption spectra were obtained using a Cary Model 14 spectrometer equipped with a thermostated cell compartment. ^1H NMR measurements were made using Varian XL-100 and HFT-80 spectrometers. Organic reaction products were identified by TLC, NMR, IR (Perkin-Elmer Model 237), and mass spectrometry (AEI MS-30 double-focusing mass spectrometer). High-resolution mass spectrometry was used to confirm the major products. Quantitative analysis of organic products was performed on a Varian Aerograph Model A 90-P3 gas chromatograph with a 5% OV-101/Chromosorb G column at 210 °C.

Photochemical Reactions. All photolyses were carried out in quartz vessels under an atmosphere of purified N_2. Quantum yields were measured in 1-cm quartz cells at 30 °C using a 100-W Hanovia Hg-vapor lamp, type SH, with the sample housed in a thermostated box equipped with a magnetic stirrer. For large-scale reactions a 450-W Hanovia lamp, type L, was used. In these reactions, photolysis was performed through a small slit in a black metal box, with the vapor phase covered with double layers of dark cloth in order to eliminate photolysis of the vapor phase. The approximate temperature was 25 °C.

Filters. For quantum yield determinations, interference filters were used to select nearly monochromatic radiation. The 366-, 313-, and

265-nm bands were isolated using Optics Technology filters 370, 330, and 270, respectively. These filters have band maxima (half-bandwidths) of 368 (34), 322 (34) and 273 (21) nm. The intensities of the filtered light were determined by ferrioxalate actinometry.[45] For large-scale photolyses, cutoff filters were used, except where noted, to eliminate high-energy radiation and to minimize solvent photolysis. Corning filters 7740, 7058, and 7910, having respective UV cutoffs at 272, 238, and 217 nm, and Vycor, with a cutoff of 222 nm, were used.

Quantum Yield Calculations. The concentrations of reactants were determined by monitoring UV–vis spectra at appropriate wavelengths. The wavelengths used in these calculations were as follows. Fe(R$_2$dtc)$_3$ 480, 444, 350, and 313 nm; Fe(Et$_2$dtc)$_2$Cl 525 and 440 nm; Fe(Et$_2$dtc)$_3$BF$_4$ 580, 540, and 480 nm; NaEt$_2$dtc, Et$_4$tds 300 nm; Fe(Et$_2$dtc)$_2$(tfd) 650, 580, and 480 nm. Where possible, simultaneous equations using absorbance data and extinction coefficients at two different wavelengths were solved and compared with calculations using only one wavelength. In all cases, concentrations determined by solving simultaneous equations agreed with values obtained from single wavelengths within experimental error. The quantum yield for the disappearance of C$_6$H$_5$SC(S)NEt$_2$, II, in pentane was determined by GLC: a solution of the thioester was photolyzed in a quartz cell, and samples were removed periodically via syringe and injected into the gas chromatograph. Integration of the resulting peaks yielded concentrations for both the disappearing thioester II and the major photolysis product, C$_6$H$_5$SSC$_6$H$_5$. All quantum yields were measured at 30.0 °C and for reaction to 20% of completion or less. Quantum yields reported are based on the decrease in concentration of reactant.

Photochemical Reaction of Fe(Et$_2$dtc)$_3$ with Chlorobenzene. Fe(Et$_2$dtc)$_3$, 357.5 mg, and 443 mg of chlorobenzene were dissolved in 245 mL of acetonitrile in a quartz flask in the dark. The solution was thoroughly degassed and placed under an atmosphere of purified N$_2$. The solution was photolyzed using a 450-W Hg-vapor lamp and a Corning filter No. 7910 having a UV cutoff of 217 nm. Samples were withdrawn periodically by syringe, the solvent was pumped off, and the residue was extracted with pentane. The pentane-insoluble residue was dissolved in CHCl$_3$, and the UV–vis spectrum was used to determine the percent conversion of Fe(Et$_2$dtc)$_3$ to Fe(Et$_2$dtc)$_2$Cl. The pentane extract was analyzed by GLC for organic products. The results are shown in Table II.

Photochemical Reaction of Fe(Et$_2$dtc)$_2$(tfd) with Chlorobenzene. Fe(Et$_2$dtc)$_2$(tfd), 100.5 mg, and 450 mg of chlorobenzene were dissolved in 30 mL of acetonitrile and thoroughly degassed. The solution was photolyzed, using an Ace Model 2130 photochemical immersion lamp which emits primarily at 254 nm. After ~90% conversion of Fe(Et$_2$dtc)$_2$(tfd) to Fe(Et$_2$dtc)$_2$Cl (measured by UV–vis spectrometry), the solvent was pumped off. The residue was extracted with petroleum ether, the ether was pumped off, and the oily residue was analyzed by mass spectrometry and GLC (see text).

Photochemical Reaction of Et$_4$tds with Chlorobenzene. Et$_4$tds, 85.0 mg, and 160 mg of chlorobenzene were dissolved in 40 mL of CH$_3$CN in a quartz flask, thoroughly degassed, and placed under an atmosphere of purified N$_2$. The sample was photolyzed using a Corning filter No. 7740 having a UV cutoff of 272 nm to filter out high-energy radiation from a 450-W Hg-vapor lamp. Samples were removed periodically via syringe. The extent of reaction was determined by measuring the absorbance of suitably diluted samples at 300 nm. Organic products were obtained by pumping off the solvent and dissolving the residue in CHCl$_3$. This solution was then analyzed by GLC.

Photochemical Reaction of NaEt$_2$dtc with Chlorobenzene. NaEt$_2$dtc, 81.7 mg, and 560 mg of chlorobenzene were dissolved in 30 mL of CH$_3$CN in a quartz flask. The solution was thoroughly degassed and placed under an atmosphere of purified N$_2$. This solution was photolyzed with a 450-W Hg-vapor lamp, using a Corning filter No. 7740 having a UV cutoff of 272 nm. Samples were removed periodically via syringe. The concentration of NaEt$_2$dtc remaining in solution was obtained by measuring the absorbance of a diluted portion of the extracted solution at 300 nm. The remainder of the sample was analyzed for organic products as before using GLC.

Photolysis of C$_6$H$_5$SC(S)N(C$_2$H$_5$)$_2$. A solution containing 2.16 mg/mL of C$_6$H$_5$SC(S)N(C$_2$H$_5$)$_2$ in pentane was degassed and transferred to a 1-cm quartz cell having a volume of 3 mL. The solution was then photolyzed using unfiltered light from a 100-W Hg lamp. Samples were withdrawn via syringe at appropriate intervals and injected into a gas chromatograph for analysis. The results are shown in Table III.

Difference Spectra (for CTTS bands). Solutions of ca. 10^{-4} M of equal concentrations of Fe(Et$_2$dtc)$_3$ in CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$, and CH$_3$CN were prepared in the dark. The differences in the electronic spectra in these solvents were determined as follows: Two 1-cm cells were placed in the reference beam of the spectrophotometer, one containing the Fe(Et$_2$dtc)$_3$ solution in CH$_3$CN, the other containing pure chlorocarbon solvent. Two cells were also placed in the sample beam, one containing Fe(Et$_2$dtc)$_3$ in chlorocarbon solvent, the other containing pure CH$_3$CN. The electronic spectrum was then taken at 30 °C and overlaid on a baseline spectrum (containing pure solvents in all four cells) to determine the positions and magnitudes of bands present in the chlorocarbon solvents but absent in CH$_3$CN. The experiment was repeated several times for each solvent combination. A typical difference spectrum is shown in Figure 2.

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Registry No. Fe(Et$_2$dtc)$_3$, 13963-59-2; Fe(pyrrdtc)$_3$, 21288-86-8; Fe(Oct$_2$dtc)$_3$, 67904-84-1; [Fe(Et$_2$dtc)$_3$]BF$_4$, 35270-33-8; Fe(Et$_2$dtc)$_2$(tfd), 25971-39-5; Fe(Et$_2$dtc)$_2$Cl, 36759-32-7; NaEt$_2$dtc, 148-18-5; I, 97-77-8; II, 3052-73-1; IV, 882-33-7; C$_6$H$_5$Cl, 108-90-7; aniline, 62-53-3.

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(16) When neat chlorobenzene was used as the solvent, significant amounts of chlorobiphenyls were also formed, as well as traces of biphenyl and several chlorine-containing compounds of high molecular weight. These products have previously been reported in the photolysis of pure chlorobenzene.[14] When the experiments were performed using acetonitrile as solvent and diluting the chlorobenzene so that >95% of the incident light was absorbed by the Fe(Et$_2$dtc)$_3$, the amount of chlorobiphenyls produced was reduced to a trace, while the yield of thioester II and phenyl disulfide IV remained unchanged.

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Organometallic Nitrosyl Chemistry. 6.[1] Cyclopentadienylnitrosyl Complexes of Chromium

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The photoinduced reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ with gaseous nitric oxide in hexanes produces a mixture of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ (major product). The same organometallic compounds can be obtained more conveniently, in better overall yields, by treating photogenerated $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O)$ with NO in tetrahydrofuran. They also occur as minor products when $(\eta^5\text{-}C_5H_5)_2Cr$ reacts with NO in hexanes, the principal product being $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$ which can be isolated in 35% yield. Their formation in these conversions can be rationalized in terms of the reactive intermediate $(\eta^5\text{-}C_5H_5)Cr(NO)_2\cdot$.

Introduction

In previous papers in this series we have outlined several general preparative routes that lead to neutral organometallic nitrosyl compounds in high yields. The principal pathways involve the treatment of anionic[2] or neutral[2,3] carbonyl complexes with nitrosyl chloride. Another potentially general method for the synthesis of these nitrosyl complexes is the reaction of nitric oxide with electron-deficient or coordinatively unsaturated organometallic compounds. The latter classification of reactants encompasses those species in which the metal attains coordinative unsaturation during thermolysis or photolysis. Some reactions of this type have been individually reported previously,[4] but a systematic study of these transformations has not yet been carried out.

We have now initiated such a study, and in this paper we describe new reactions between nitric oxide and the cyclopentadienylchromium complexes $(\eta^5\text{-}C_5H_5)_2Cr$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. The chromium systems were chosen as a convenient starting point because of our familiarity with cyclopentadienylchromium nitrosyls acquired during our earlier work.[2,3,5]

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Nitric oxide (Matheson CP grade, 99.0% minimum) was further purified by passing it through a column of activated silica gel maintained at −78 °C. A mass spectrum of the effluent gas exhibited only a sharp peak at m/e 30 assignable to NO^+; it did not exhibit peaks attributable to ions such as NO_2^+ or N_2O^+. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton and carbon-13 magnetic resonance spectra were recorded on Varian Associates T60 and CFT20 spectrometers, respectively, with tetramethylsilane being employed as an internal standard. The low-resolution mass spectra were taken at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method with the assistance of Dr. G. K. Eigendorf and Mr. J. W. Nip. Elemental analyses were carried out by Mr. P. Borda of this department.

Reaction of Nitric Oxide with $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O)$. A stirred orange solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[6] (1.02 g, 5.03 mmol) in tetrahydrofuran (250 mL) was irradiated for 0.5 h in a photoreactor using a medium-pressure mercury lamp (Hanovia L-450W) housed in a water-cooled Pyrex immersion well. [Monitoring of several runs by infrared spectroscopy indicated these to be the most efficient conditions for generation of the desired reactive intermediate.] Prepurified nitric oxide was gently bubbled through the resulting red-black solution for 1 h at room temperature, and the solvent was removed from the reaction mixture in vacuo. The remaining dark green residue was redissolved in a minimum of dichloromethane (∼10 mL), and the solution was transferred by syringe onto a short (3 × 5 cm) Florisil column. Elution of the column with dichloromethane developed a red-orange band that was collected and taken to dryness in vacuo. Sublimation of the residue at room temperature (5×10^{-3} mm) onto a dry ice cooled probe afforded 0.20 g of unreacted $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. The involatile red-violet solid remaining (∼0.01 g) was identified by its infrared spectrum as $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$.[7]

The Florisil column was then eluted with tetrahydrofuran to produce a dark green band which was also collected and taken to dryness in vacuo. Crystallization of the resulting solid from dichloromethane–hexane yielded green crystals (0.38 g, 42% yield based on unrecovered starting material) of analytically pure $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$: ν_{NO} (in CH_2Cl_2) 1825, 1719 cm^{-1}; proton NMR δ (in $CDCl_3$) 5.78 (s); mp (in air) 86–87 °C. Anal. Calcd for $C_5H_5CrN_3O_4$: C, 26.92; H, 2.26; N, 18.83. Found: C, 27.21; H, 2.15; N, 18.76.

The Photonitrosylation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. A stirred solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (1.50 g, 7.39 mmol) in hexanes (200 mL) was irradiated as described above while a slow stream of prepurified nitric oxide was passed through the reaction mixture. After 1 h the color of the solution had changed to brown-red, and a green-brown precipitate had formed. An infrared spectrum of the solution showed an ∼40% decrease in intensity of the carbonyl and nitrosyl absorptions due to the initial reactant. Irradiation for an additional 1 h diminished the amount of starting material by a further 10%, and at this point the reaction was stopped. The reaction mixture was purged with N_2, and the solid was allowed to settle. The supernatant hexane solution was decanted and taken to dryness in vacuo to obtain a red-brown residue. This residue was chromatographed

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