The photosolvation of $[Fe(TIM)MeCN(CO)]^{2+}$ in acetonitrile shows no temperature dependence over the temperature range studied, 10–25 °C. The lack of an observed temperature dependence may be due to the small temperature range examined. If the excited-state activation energy is small, the change of k_r over the temperature range studied could be insignificant.

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Registry No. $[Fe(TIM)CH_3CN(CO)](PF_6)_2$, 43223-43-4; $[Fe(TIM)(P(OEt)_3)_2](PF_6)_2$, 64070-43-5; $[Fe(TIM)(CH_3CN)_2](PF_6)_2$, 43223-41-2; $[Fe(TIM)(im)_2](PF_6)_2$, 43223-42-3; $[Fe(TIM)(NH_3)_2](PF_6)_2$, 64070-41-3; $[Fe(TIM)(py)_2](PF_6)_2$, 64070-39-9.

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Charge-Transfer Photochemistry of Halonitrosylbis(*o*-phenylenebis(dimethylarsine))iron(II)

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Charge-transfer band irradiation of solutions of $[Fe^{II}X(NO)(das)_2](ClO_4)_2$ (X = Cl, Br, or I and das = *o*-phenylenebis(dimethylarsine)) in acetone, acidified methanol, and acidified methanol containing excess halide ions produces $[Fe^{III}X_2(das)_2]^+$. The quantum yield is independent of wavelength (255, 313, 366, 405, and 435 nm), the concentration of starting material, the incident light intensity, and the concentration of halide ion. However, the quantum yield is sensitive to the solvents and to the halide ligands. The photoactive excited state is assigned to the $b_2(d_{xy}) \rightarrow e(\pi^*(NO))$ transition which causes the formal oxidation of Fe(II) to Fe(III) and the formal reduction of NO^+ to NO radical. Mechanisms of the reaction are discussed.

The photoreactivity of charge-transfer excited states of transition-metal complexes is poorly understood in comparison with the photoreactions originating from ligand field excited states.[1] Whereas the latter excited states most commonly lead to ligand labilization[1] caused by population of metal–ligand antibonding orbitals, the former can lead to photoredox processes in addition to ligand labilization. For example, photoexcitation into ligand to metal charge-transfer (LTMCT) excited states of tris(dithiocarbamato)iron(III) complexes led to a series of reactions which were interpreted in terms of free radical ligands and a reduced metal center in the excited state.[4–6] Similarly, the metal to ligand charge-transfer (MTLCT) photochemistry of hexakis(aryl isocyanide) complexes of group 6B metals was interpreted in terms of a formally oxidized metal center.[7] The charge-transfer photochemistry of complexes containing more classical ligands has recently been reviewed.[1]

Low-lying MTLCT excited states are in general expected in complexes containing good π-acceptor ligands which are coordinated to metals in low oxidation states. The nitrosyl ligand was chosen for study because it fulfills the qualities of being a good π acceptor. Although the ground-state properties of metal nitrosyl complexes have been well studied and are well explained by the Enemark–Feltham theory,[8] excited-state properties have not received much attention. Quantitative studies of the photochemistry of nitrosyltetracarbonylmanganese[9] and pentacyanonitrosylferrate[10] have been reported. The former compound undergoes photosubstitution

Table I. Electronic Absorption Spectra of $[Fe(das)_2(NO)X](ClO_4)_2$

Complexes	λ_{max}, μm^{-1} (molar absorptivity, $M^{-1}\ cm^{-1}$)[a]		
	I	II	III
X = Cl	3.86 (1.38×10^4)	3.19 (1.84×10^4)	2.50 (4.34×10^3)
X = Br	3.58 (1.96×10^4)	3.08 (1.41×10^4)	2.53 (2.65×10^3)
X = I	3.28 (2.26×10^4)	2.48 (5.23×10^4)	2.07 (1.33×10^3)

[a] Measured in methanol

with loss of carbon monoxide, while the latter undergoes expulsion of nitric oxide. We report here the photochemistry of the mixed-ligand complex chloronitrosylbis(*o*-phenylenebis(dimethylarsine))iron(II), $[FeCl(NO)(das)_2]^{2+}$.

Experimental Section

Compounds. $[FeCl(NO)(das)_2](ClO_4)_2$ (yellowish orange) and $[FeI(NO)(das)_2](ClO_4)_2$ (purple) were kindly supplied by Professor Robert D. Feltham, University of Arizona. $[FeBr(NO)(das)_2](ClO_4)_2$ was prepared by adding excess bromide ion to a methanol solution of the chloro complex.[11] $[FeCl_2(das)_2]Cl$ and $[FeBr_2(das)_2]Br$ were synthesized by adding a benzene solution of the stoichiometric amount of the diarsine to a benzene solution of $FeCl_3$ or $FeBr_3$, respectively, with stirring in a drybox as described by Nyholm.[12] Methanol and acetone (Mallinckrodt, Spectra AR) were redistilled before use.

Instrumentation. The electronic absorption spectra and the absorbance changes for the quantum yield measurements were taken using a Cary 14 spectrometer and a Hitachi Perkin-Elmer 139 UV–vis spectrometer. Infrared spectra were recorded using a Perkin-Elmer Model PE-421 grating infrared spectrophotometer.

Photolysis was carried out using an optical train consisting of a Hanovia 100-W high-pressure quartz mercury vapor lamp (SOL-608A) with interference filters for appropriate wavelength selection. The photolysis wavelengths and the filter combinations were the following: 255 nm, interference filter with 16.2% maximum transmittance; 313 nm, interference filter with 14.1% maximum transmittance; 366 nm, chemical filter solutions of $CoSO_4 \cdot 7H_2O$ (45 g/100 mL of H_2O, 10 cm) and 2,7-dimethyl-3,6-diazacycloheptal-1,6-diene perchlorate (0.02 g/100 mL of H_2O, 1 cm) with 47% transmittance; 405 nm, Corning glass filter 4-15 and solutions of I_2/CCl_4 (0.75 g/100 mL of CCl_4, 1 cm) and CH_3NO_2/H_2O (saturated solution, 10 cm) allowing 25% transmittance; 435 nm, Corning glass filter 4-75 and filter solution of $NaNO_2$ (saturated solution, 1 cm) with 33% transmittance.

Photochemical Studies. Constant geometry was obtained by mounting the source, filters, and cells on an optical bench. A 1-cm quartz photolysis cell with a volume of 3 mL was used.

The light intensity was measured using ferrioxalate actinometry as described by Calvert and Pitts.[13] Each actinometric run was made after the lamp had reached a stable and efficient operating temperature. Runs were made before and after the photochemical study. The light intensity varied within ±3% after several hours' operation. The average light intensity was used to calculate the quantum yield. The incident light intensity was 2.26×10^{15} quanta/s at 366 nm, 2.53×10^{14} quanta/s at 255 nm, and 9.15×10^{14} quanta/s at 435 nm. The photolyses were conducted to less than 5% for the actinometric run and less than 15% for the photochemical studies.

The quantum yield of product formation was calculated by monitoring the appearance of an intense absorption peak of the product at 550, 605, and 768 nm for $[FeCl_2(das)_2]^+$, $[FeBr_2(das)_2]^+$, and $[FeI_2(das)_2]^+$, respectively. The quantum yield for decrease of the starting material was calculated by following the disappearance of the charge-transfer band at 400, 420, and 483 nm, which is characteristic of $[FeX(NO)(das)_2](ClO_4)_2$, $X^- = Cl^-$, Br^-, and I^-, respectively.

Results

Electronic Spectra. The electronic absorption spectra of $[FeX(NO)(das)_2](ClO_4)_2$, ($X^- = Cl^-$, Br^-, and I^-) in methanol consist of three intense, well-resolved bands in the visible and near-UV regions. The band maxima and molar absorptivities are given in Table I. Note that the two lowest energy bands, labeled bands II and III in Table I, are red shifted between 0.1 and 0.3 μm^{-1} as the halide is changed from chloride to iodide. No solvent-induced shift of the lowest energy band is observed when the solvent was changed to acetone. Bands I and II cannot be observed in acetone because of solvent absorption. In addition to the well-defined bands, several poorly resolved features are observed. In the chloro complex, a shoulder at 275 nm is observed on the intense 259-nm band. In the bromo complex, a shoulder at 240 nm is observed on the 260-nm band. In the iodo complex, a shoulder at 388 nm is observed on the 353-nm band. A careful search of the long-wavelength side of the spectra of the chloro and bromo complexes failed to reveal any d–d bands. If any such features do exist, their molar absorptivities are less than 1.

Photochemistry. All of the complexes investigated in this study were photoactive in methanol and acetone when irradiated at 255, 313, 366, 405, and 435 nm. In all cases, the photoreaction caused decreases in the intensities of the charge-transfer bands characteristic of the starting material. Typical spectral changes are shown in Figure 1.

When $[FeCl(NO)(das)_2]^{2+}$ was irradiated in acidified methanol containing an excess of chloride ion, the spectral changes shown in Figure 1a were observed. Isosbestic points were found at 490, 390, and 345 nm. The photoproduct is $[FeCl_2(das)_2]^+$. It was identified by comparison of its infrared and electronic absorption spectra with those of independently synthesized samples.[12] The reaction proceeds with a 1:1 stoichiometry of photoproduct produced to reactant lost as calculated from the known molar absorptivities of the starting material and photoproduct. In contrast, when the reaction was carried out in methanol with no acidification and without excess free chloride ion, the spectral changes shown in Figure 1b were observed. The changes are indicative of disappearance of the starting material without production of the iron(III) product. This reaction was not studied further.

When $[FeCl(NO)(das)_2]^{2+}$ was irradiated in acetone or in acidified methanol with no excess chloride ion, the spectral changes shown in Figure 1c were observed. The photoproduct again is $[FeCl_2(das)_2]^+$, but isosbestic points are found at 500, 378, and 355 nm. Calculation of the concentration changes using the known molar absorptivities of the starting material and the photoproduct indicated that the stoichiometry of the reaction was 1 mol of photoproduct to 2 mol of starting material lost. This reaction provides an interesting example of a case where isosbestic points are required by the fixed relationship between the product and the reactant even though the stoichiometry is not 1:1.[14]

The bromo and iodo complexes exhibited photoreactivity similar to that of the chloro complex. The photochemistry of the bromo complex exactly parallels that of the chloro complex with formation of $[FeBr_2(das)_2]^+$ in the presence of excess bromide ion and disappearance of the starting material without production of a species absorbing in the visible region of the spectrum when excess bromide ion is lacking. Isosbestic points were observed in the spectra similar to those observed in the chloride reactions. In contrast, irradiation of the iodo complex produced an unstable complex which was rapidly reduced thermally to $[FeI_2(das)_2]$. Interestingly, the mixed halo complexes $[FeXY(das)_2]^+$ could be readily prepared by irradiation of $[FeX(NO)_2(das)_2]^{2+}$ in acidified methanol with an excess of a different halide ion Y^-.

The quantum yields for the reactions of $[FeX(NO)(das)_2]^{2+}$ are given in Table II. The quantum yields for the chloro complexes were wavelength independent between 255 and 435 nm. The reaction quantum yields decreased in the order $Cl^- > Br^- > I^-$.

The effects of various aspects of the medium on the quantum yields were also examined. Within the experimental error of the measurement (±10%), the quantum yields were independent of the chloride ion concentration, starting material

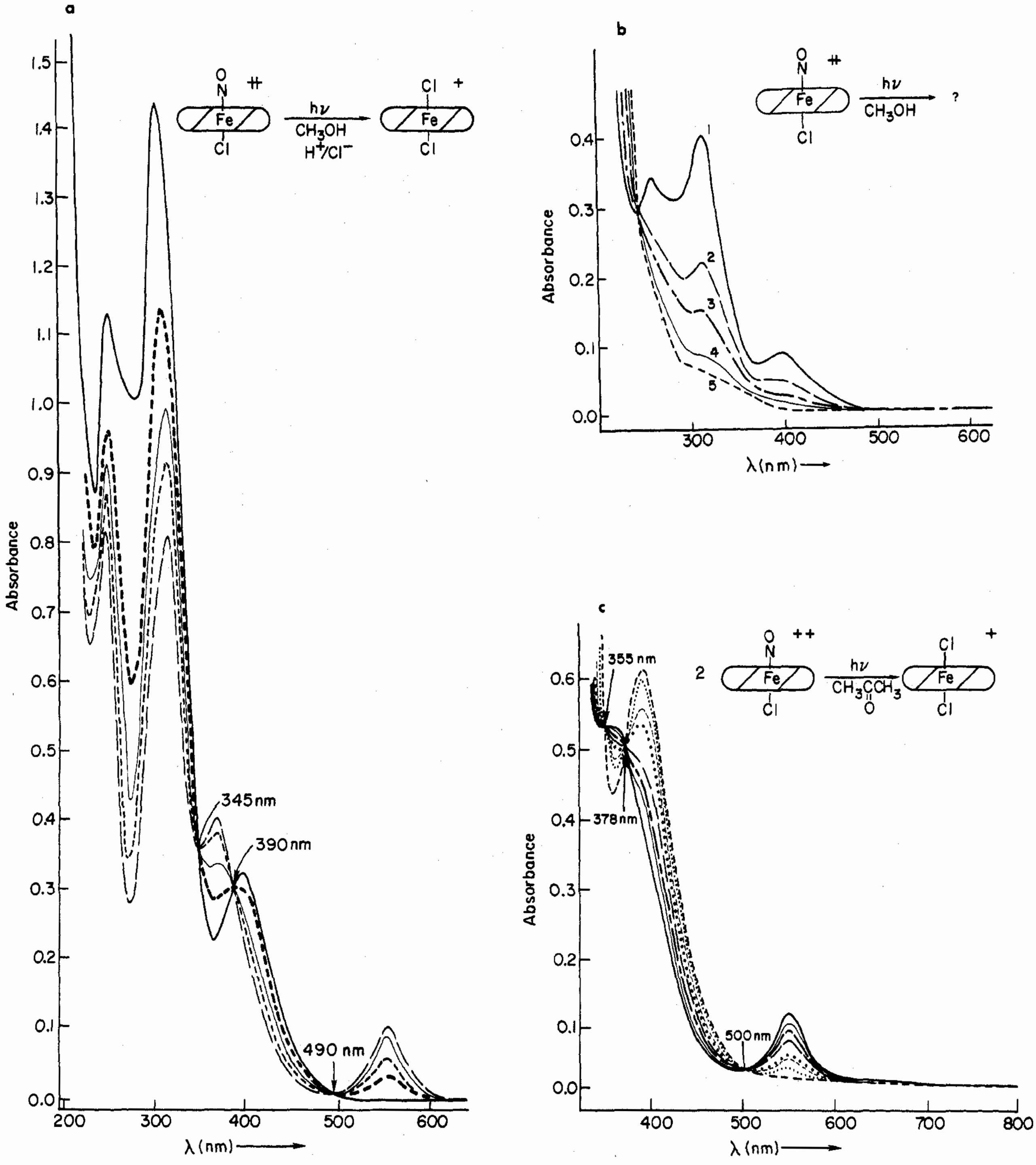


Figure 1. Electronic spectral changes accompanying irradiation of $[Fe(das)_2(NO)Cl]^{2+}$ at 360 nm. (a) Acidified methanol containing excess chloride ion: —, 0 min; ---, 5 min; —, 10 min; ---, 15 min; – – –, 20 min; at 7.296×10^{-5} M. (b) Methanol solution: 1 = 0 min; 2 = 10 min; 3 = 20 min; 4 = 30 min; 5 = 55 min; at 2.028×10^{-5} M. (c) Acetone solution: ---, 0 min; ····, 5 min; ---, 10 min; ····, 15 min; – – –, 20 min; —-—, 25 min; —, 30 min; —, 40 min; at 1.413×10^{-4} M.

concentration, incident light intensity, and oxygen concentration in acetone. The chloride ion concentration was varied over the range 1×10^{-5} to 8.5×10^{-3} M without changing the quantum yield of formation of $[FeCl_2(das)_2]^+$. We also found that the trace amounts of chloride ion (estimated to be on the order of 10^{-4} M) introduced into methanol by acidifying the solvent with perchloric acid and acetic acid did not affect the quantum yield. All of the above tests were run with the initial concentration of the nitrosyl complex between 4×10^{-5} and 1.5×10^{-4} M. No quantum yield variation was found over this range of starting material concentration. The range of light intensities tested varied from 2.7×10^{14} to 8.6×10^{15} quanta/s. In order to determine if oxygen affected the reaction, acetone solutions were deoxygenated by bubbling nitrogen gas through them for 1 h. The quantum yields were unchanged.

The reaction was sensitive to the solvent. In methanol, the quantum yields for product formation were 0.23 ± 0.03, while in acetone the quantum yields were 0.10 ± 0.02. The reaction was very sensitive to water. In acetone, the formation of $[FeCl_2(das)_2]^+$ decreased as the water concentration increased and was completely inhibited when the ratio of water con-

Table II. Quantum Yields of Photoreaction of $[Fe(das)_2(NO)X](ClO_4)_2$

Complex	Conditions	Wavelengths, nm	Quantum yield	
			ϕ_{formn}[a]	$\phi_{decrease}$[a]
X = Cl	$CH_3OH/H^+/Cl^-$	255	0.24 ± 0.03	0.24 ± 0.03
		313	0.21 ± 0.03	0.21 ± 0.03
		366	0.25 ± 0.03	0.25 ± 0.03
		405	0.24 ± 0.04	0.23 ± 0.04
		435	0.24 ± 0.02	0.24 ± 0.02
	CH_3OH/H^+	255	0.23 ± 0.04	0.46 ± 0.04
		313	0.20 ± 0.03	0.40 ± 0.03
		366	0.21 ± 0.03	0.42 ± 0.03
		405	0.22 ± 0.03	0.44 ± 0.03
		435	0.21 ± 0.03	0.43 ± 0.03
	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	255	*b*	*b*
		313	*b*	*b*
		366	0.12 ± 0.02	0.24 ± 0.02
		405	0.10 ± 0.02	0.21 ± 0.03
		435	0.09 ± 0.03	0.20 ± 0.03
	$CH_3\overset{\overset{O}{\|}}{C}CH_3/N_2$	405	0.12 ± 0.02	0.23 ± 0.03
		435	0.11 ± 0.03	0.23 ± 0.03
	CH_3OH	255	*c*	0.25 ± 0.03
		313	*c*	0.25 ± 0.02
		366	*c*	0.25 ± 0.02
		405	*c*	0.23 ± 0.04
		435	*c*	0.22 ± 0.03
X = Br	$CH_3OH/H^+/Br^-$	435	0.12 ± 0.03	0.12 ± 0.03
X = I	CH_3OH/H^+	435	<0.06	<0.12

[a] ϕ_{formn}: quantum yield of photoproduct formation. $\phi_{decrease}$: quantum yield of decrease of starting material. [b] Strong solvent absorption prohibits quantum yield measurements. [c] In CH_3OH, only a species absorbing at λ <400 nm was formed. ϕ_{formn} cannot be calculated.

centration to complex concentration was greater than 5×10^5.

No thermal reactions were observed in acetone or acidified methanol. In the presence of water or nonacidified methanol a thermal reaction occurred giving the same spectral changes as the photochemical reaction.

Discussion

1. Proposed Assignments of the Electronic Absorption Bands. The three-band electronic absorption spectra observed for the $[FeX(NO)(das)_2]^{2+}$ complexes are assigned to charge-transfer and internal ligand transitions on the basis of the large molar absorptivities of all of these bands ($\epsilon > 10^3$). In the case of the charge-transfer transitions, both ligand to metal charge transfer (LTMCT) and metal to ligand charge transfer (MTLCT) must be considered. The optical electronegativities of the ligands are the following: Cl^-, 3.0; Br^-, 2.8; I^-, 2.5; das, 2.46.[15] Using these values as a guide, it is reasonable to expect that the lowest energy LTMCT will be das to metal in character. In the case of MTLCT, experience has shown that the π antibonding orbitals of the nitrosyl ligand are often lower in energy than the d_{z^2} and $d_{x^2-y^2}$ orbitals.[8] Thus, the lowest energy MTLCT most likely will be d_{xy} to π*(NO) or d_{xz}, d_{yz} to π*(NO) in character. The internal ligand transitions are more difficult to assign, but they can often be confidently assigned on the basis of transitions observed in the free ligands and/or transitions observed in other metal complexes containing the same ligands.

We assign the lowest energy band (labeled band III in Table I) to the d_{xy} to π*(NO) MTLCT transition. From experience with similar compounds, it is reasonable to expect that the π*(NO) orbital will be the LUMO. The observed energies of this band are in the same region as the d to π*(NO) bands previously assigned in $[Fe(CN)_5(NO)]^{2-}$ (band maximum 2.01 μm^{-1})[16] and $[RuCl(NO)(NH_3)_4]^{2+}$ (band maximum 2.27 μm^{-1}).[17] The d_{xz} and d_{yz} orbitals are probably lower in energy than d_{xy} because NO is an excellent π acceptor.

The observed halide dependence of band III is a consequence of the ligand inductive effect and the halide p π component in the molecular orbital which is primarily π*(NO) in character. As the halide is changed from chloride to iodide, the σ- and π-donor properties decrease.[18] The latter change decreases the halide participation in the three-center π MO and lowers the energy of the empty orbital which is primarily π*(NO). The former change causes a decrease in the effective 10*Dq* along the axis and slightly raises the energy of the d–π orbitals. The intensity of band III decreases in the order Cl^- (ϵ 4.3 × 10^3) > Br^- (ϵ 2.7 × 10^3) > I^- (ϵ 1.3 × 10^3). The magnitude and ordering of the intensities are consistent with intensity borrowing from bands II and I.[19] In both the ruthenium[17] and iron[16] studies referred to previously, the molar absorptivities for the $d_{xz} \rightarrow \pi^*(NO)$ transition were less than 5×10^1 and the nearest intense charge-transfer bands were greater than 1.5 μm^{-1} to high energy. In $[FeX(NO)(das)_2]^{2+}$, the nearest intense band (band II) is 0.69 μm^{-1} (Cl^-), 0.73 μm^{-1} (Br^-), and 0.77 μm^{-1} (I^-) to higher energy. Thus an intensity borrowing mechanism is consistent with the observed intensity decrease as a function of the halide ion.

Two assignments are reasonable for band II: arsine to π*(NO) charge transfer or d_{xz}, d_{yz} to π*(NO) charge transfer. Three observations regarding the orbital energies are relevant. First, the energy change caused by changing the halide is almost the same as that for band III. A similar change is expected for charge transfer from the arsine because both the arsine σ-donor orbitals and the d_{xy} orbital are in the plane of the complex and are orthogonal to the halide donor orbitals. A larger change would be expected if the transition were from the d_{xz}, d_{yz} orbitals which are directly involved in π interactions with the halide. The major cause of the energy change would be the change of the LUMO which consists primarily of π*(NO) character but which also involves halide p–π and metal d_{xz} and d_{yz} character. Second, the energy difference between bands II and III is on the order of 0.7 μm^{-1}. If band II were assigned as d_{xz}, d_{yz} to π*(NO), the energy gap between d_{xy} and d_{xz}, d_{yz} would have to be about 0.7 μm^{-1}. In $[Fe(CN)_5(NO)]^{2-}$, the gap is 0.53 μm^{-1} and in $[RuX(NO)(NH_3)_4]^{2+}$ the gap was not reported. The 0.7-μm^{-1} separation is large but not impossible in a complex containing a very strong π-acceptor ligand such as NO. Third, the transition energy is low for a transition originating on the arsenic donor atoms. On the basis of optical electronegativities, we calculate that it should occur above 40 μm^{-1}. From the above arguments, we favor the d_{xz}, d_{yz} to π*(NO) ($e \rightarrow e$) assignment.

The highest energy band, band I, is readily assigned as an internal ligand transition in the das ligand. The most telling evidence for this assignment is the presence of a band of identical energy in the iron(III) complexes $[FeX_2(das)_2]^+$. In addition, the free ligand has an absorption maximum in this region. The latter observation suggests that the internal transition is $\pi \rightarrow \pi^*$.

We do not assign any bands to halide to metal charge transfer because the maximum observed change in energy of the bands is only 0.15 μm^{-1} as the halide is changed from chloride to bromide, and 0.28 μm^{-1} as it is changed from bromide to iodide. For halide to metal charge-transfer transitions, the change is usually greater than 0.47 μm^{-1} between Cl^- and Br^- and greater than 0.57 μm^{-1} between Br^- and I^-.[17,20]

2. Excited-State Origin of the Photoreactions. The observed photochemistry can be simply explained in terms of the bonding properties of the orbitals involved in the charge-transfer excited states. Because of the wavelength independence of the reaction quantum yield, the photochemistry must be interpreted in terms of the lowest energy excited state,

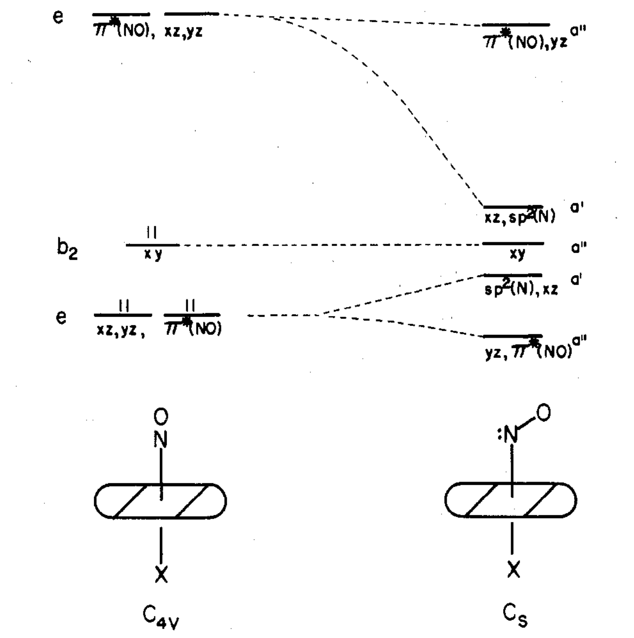


Figure 2. Simplified correlation diagram for the linear and bent coordinated nitrosyl.

which we have assigned as metal d to π^*(NO) MTLCT. In the one-electron transition, the metal is formally oxidized and the NO ligand formally reduced. In the MO description of Enemark and Feltham,[8] the transition is b_2 to e (Figure 2). In the more familiar but less precise description, the transition is from the d orbital of an iron(II) to the empty π antibonding orbital of a NO^+ ligand. The result in either case will be a charge separation which reduces electron density on the iron and increases electron density on the nitrosyl. The subsequent scavenging leaves behind an iron(III) fragment.

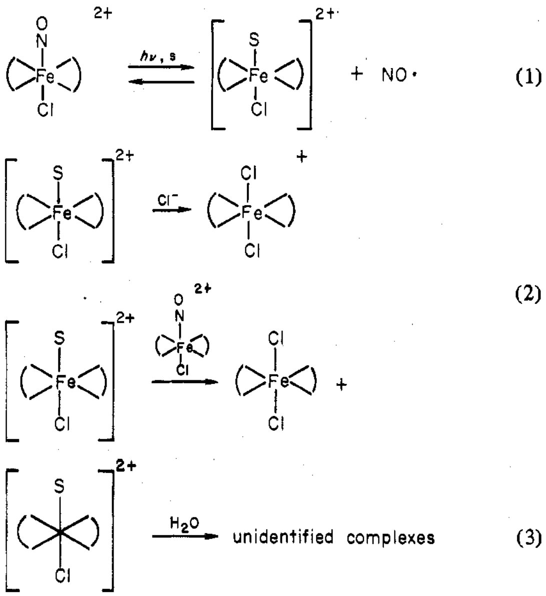
The effects of the charge-transfer transition on the bonding within the molecule are metal–nitrosyl bond weakening with concomitant strengthening of the metal–halide and metal–arsine bonds. The depopulated orbital is nonbonding between both the metal and the halogen and the metal and the nitrosyl. The arsine ligands could function as π acceptors, in which case the depopulated orbital would be π bonding between the metal and the arsine. However, it has been argued that the arsine ligand is not a good π acceptor.[21] Thus, the metal–arsine bonding changes in the transition are probably very small. The orbital which is populated in the transition is strongly metal–nitrosyl antibonding. The formal oxidation of the metal will further decrease the metal–nitrosyl π interaction but will increase the metal–halide interactions. Thus, the net bonding changes will be strong metal–nitrosyl bond weakening, moderate metal–halide bond strengthening, and very little metal–arsine bond change. These expectations are consistent with the observed NO loss and Fe(III) photoproduct.

In concert, the electron transfer and bonding changes provide an explanation for the observed photoactivity. The $[FeX(NO)(das)_2]^{2+}$ complexes provide another illustration of the close connections between spectroscopy, simple MO theory, and charge-transfer photochemistry.

3. Mechanism of the Photoreaction. Two observations suggest that the photoreactions occur from a common intermediate: (1) the quantum yield for disappearance of the starting material is independent of the concentration of chloride ion and (2) the quantum yield is independent of the starting material concentration. In both cases, the photoproduct is an oxidized iron(III) complex. A reaction mechanism consistent with these observations is shown in Scheme I.

The primary photochemical step is formal production of a neutral NO radical. This radical is scavenged, probably by the solvent, or diffuses away, and a relatively long-lived iron(III) complex $[FeXS(das)_2]^{2+}$ is produced. This complex may be five-coordinate in analogy to the five-coordinate $[Fe(dtc)_2X]$ complexes which were found as the final photoproducts in the photochemistry of tris(dithiocarbamato)-iron(III) complexes.[5] Alternatively, it may be weakly solvated in the sixth coordination site. This intermediate rapidly reacts with halide ion to form the stable $[FeX_2(das)_2]^+$ photoproducts. In the absence of free halide ion, the intermediate attacks unreacted $[FeX(NO)(das)_2]^{2+}$ and abstracts the halide to form the $[FeX_2(das)_2]^{2+}$ photoproduct. In the presence of water at concentrations greater than 10^5 times that of $[FeCl(NO)(das)_2]^{2+}$, the intermediate reacts to produce only a compound which does not absorb at wavelengths longer than 400 nm. Smaller water concentrations lead to a mixture of products. The photoproduct with water was not characterized.

Scheme I



Because the quantum yield for formation of the photoproduct in a given solvent is constant and independent of the halide ion concentration, the quantum yield is governed by the competition between the scavenging of the reactive intermediate and the back-reaction of the Fe(III) and the NO radical to produce the starting material. The dependence of the quantum yield on the solvent suggests that the solvent plays a major role in the scavenging. Two types of scavenging could explain these observations: associative attack on the reactive intermediate by the solvent and radical scavenging of the NO. The former reaction will be referred to as a scavenging reaction although it is not the familiar radical scavenging.

The associative attack by the solvent on the reactive intermediate would be expected to be enhanced in the iron to nitrosyl charge-transfer excited state for two reasons. First, as discussed in the previous section, the charge transfer produces a formal Fe(III) intermediate. The increased formal charge would be expected to enhance nucleophilic attack by Lewis base solvents. Second, the Enemark–Feltham treatment of the energetics of the complex suggests that the nitrosyl ligand will be bent in the excited state as shown in Figure 2.[8] The e orbital populated in the excited state correlates with low-energy a and a′ orbitals in the bent C_s symmetry. The bending of the nitrosyl ligand in the excited state will increase the formal positive charge on the metal and thus further favor nucleophilic attack by the solvent.

According to the associative mechanism, a Lewis base solvent will attack the formally oxidized iron. The more rapid the attack compared to decay back to the ground state, the larger the reaction quantum yield. This expectation is consistent with the observation that the quantum yield is greatest in water, smaller in methanol, and smallest in acetone. The ligating ability of the solvents follows the same order. This mechanism does not specify the subsequent reactions of the nitrosyl radical. The associative attack by the solvent could displace NO from the coordination shell. Alternatively, a rapid radical reaction could occur between the coordinated solvent and the NO radical in close proximity. In both cases, the quantum yield is determined by the rate of the associative attack of the solvent on the metal.

The alternative mechanistic explanation of the reaction is dissociation of an NO radical to form a caged Fe(III)–NO pair. According to this mechanism, the quantum yield would be determined by the relative rate of either the scavenging of the NO or the diffusion of NO out of the cage relative to the rate of secondary recombination of the pair. The fate of the NO was not determined because of the low concentrations (10^{-4}–10^{-5} M) at which the photoreactions were studied. Solubility limitations prevent us from exploring other solvents to distinguish between these mechanisms.

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Registry No. $[Fe(das)_2(NO)Cl](ClO_4)_2$, 36236-95-0; $[Fe(das)_2(NO)Br](ClO_4)_2$, 64070-48-0; $[Fe(das)_2(NO)I](ClO_4)_2$, 64070-46-8; $[FeCl_2(das)_2]^+$, 47511-84-2; $[FeBr_2(das)_2]^+$, 47511-80-8; $[FeI_2(das)_2]^+$, 64070-44-6.

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A Resin-Bound Vanadyl Catalyst for the Epoxidation of Olefins

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Oxovanadium(IV) was incorporated on a sulfonic acid (sodium form) ion-exchange resin, and this system was found to catalyze the epoxidation of a variety of cyclic and acyclic olefins in the reaction of the olefin with *tert*-butyl hydroperoxide. The yields of epoxides formed were far greater than those catalyzed in the same reaction with the homogeneous catalyst $VO(acac)_2$, and selectivities toward the epoxide were 100%. Various factors enhancing and diminishing the yields were investigated, and longevity experiments on the catalyst showed that it could be recycled several times without noticeable decrease in activity. Experiments were carried out on various steps of the mechanism of epoxidation proposed elsewhere for the homogeneously catalyzed reaction. It was found that the kinetic results on the heterogeneous catalyst are consistent with the mechanism proposed for the homogeneous system.

Introduction

In a series of papers by Gould and co-workers, several acetylacetonato complexes of transition metals were studied as catalysts for the oxidation of cyclohexene and other cyclic olefins.[1-5] In these studies, vanadyl ion was of primary interest as the catalytic species.

Increasing interest in polymer-anchored catalysis as well as the commercial importance of epoxidation of olefins prompted us to investigate various methods of incorporation of vanadyl ion onto an immobile support. To this end we have synthesized insoluble polymers containing oxovanadium(IV) attached to acetylacetone, ethylenediamine, and pyridine ligands, which will be reported in another paper.[6] This research is concerned with the incorporation of oxovanadium(IV) onto an ion-exchange resin, evaluation of the activity of the catalyst toward epoxidation, and mechanistic aspects of the reaction.

Experimental Section

Starting Materials. Vanadyl sulfate and bis(acetylacetonato)oxovanadium(IV) were purchased from J. T. Baker and used as received. Aldrich supplied *tert*-butyl hydroperoxide, which was dried over molecular sieves and stored in the cold. Rexyn 101 (H), research grade, a sulfonic and ion-exchange resin of 40–100 mesh, was purchased from Fisher. All olefins were obtained from Aldrich, Eastman, or Chemical Samples; cyclic olefins were purified according to the method of Fusi et al.[7,8]

Physical Methods and Analyses. The epoxide products were identified by a comparison of their infrared and NMR spectral qualities, as well as gas chromatographic retention times, with those of authentic samples. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer whereas NMR spectra were obtained on a Varian A-60 spectrometer. Gas