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Photooxidation of bis(diethyldithiocarbamato)dicarbonyliron(II) in chloroform

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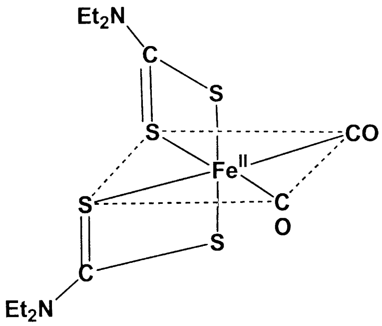
Abstract

The complex $Fe^{II}(et_2dtc)_2(CO)_2$ with et_2dtc^- (diethyldithiocarbamate) in $CHCl_3$ undergoes a photooxidation to $Fe^{III}(et_2dtc)_2Cl$ with a quantum yield of $\phi = 0.0015$ at $\lambda_{irr} = 366$ nm. It is suggested that this photoreaction originates from a ($Fe^{II} \rightarrow \pi^*$ (et_2dtc^-)) metal-to-ligand charge transfer or ligand-field excited state.

Keywords: Electronic spectra; Photooxidation; Iron complexes; Iron–sulfur compounds

1. Introduction

Iron carbonyls with sulfur ligands, such as $Fe_2(CO)_6S_2$, undergo a variety of thermal and photochemical transformations [1]. Mixed-ligand complexes of this type have been also suggested to serve as kinetically inert models for certain iron–sulfur enzymes [1]. In particular, Fe-only hydrogenase from *Clostridium pasteurianum* contains iron atoms which are octahedrally coordinated by sulfur ligands and CO (or CN^-) [2]. Although the function of natural iron–sulfur compounds is frequently related to redox changes between Fe(II) and Fe(III) [3–5], the iron–sulfur–carbonyl models are relatively redox stable [1]. However, it is conceivable that such model complexes undergo a facile electron transfer as a light-induced process. In this context it is of interest that iron–sulfur enzymes are well known to participate in photosynthesis [6]. As a promising candidate for the observation of a photoredox reaction of a simple iron carbonyl compound with sulfur ligands we selected the complex $Fe^{II}(et_2dtc)_2(CO)_2$ [7–10] with et_2dtc^- (diethyldithiocarbamate) for the present study.In the presence of a suitable electron acceptor this Fe(II) complex was expected to undergo a photooxidation to Fe(III). For this purpose we chose $CHCl_3$ as solvent which has been widely used as versatile oxidant in inorganic photochemistry [11,12].



2. Experimental

2.1. Materials

All solvents used for spectroscopic measurements were of spectrograde quality and saturated with argon. The complexes $Fe^{II}(et_2dtc)_2(CO)_2$ [7] and $Fe^{III}(et_2dtc)_2Cl$ [13] were prepared by literature procedures.

2.2. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or a Uvikon 860 absorption spectrometer. The light source used for irradiation was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using Schott PIL/IL interference filters or a Schoeffel GM/1 high-intensity monochromator (bandwidth 23 nm) with additional Schott cut-off filters to avoid short-wavelength

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and second-order irradiation. In all cases the light beam was focused on a thermostated photolysis cell by a quartz lens.

2.3. Photolyses

The photolyses were carried out in solutions of $CHCl_3$ in 1 cm spectrophotometer cells at room temperature under argon. Progress of the photolyses were monitored by UV-Vis spectrophotometry. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by ferrioxalate actinometry and equipped with a RkP-345 detector.

3. Results

Since $Fe^{II}(et_2dtc)_2(CO)_2$ is oxygen-sensitive, in particular in solution, all solvents were saturated with argon. The electronic spectrum of the complex depends only slightly on the solvent (e.g. CH_3CN, $CHCl_3$). The absorption spectrum of $Fe^{II}(et_2dtc)_2(CO)_2$ in $CHCl_3$ (Fig. 1) shows bands at $\lambda_{max} = 360$ nm ($\varepsilon = 8600\,M^{-1}\,cm^{-1}$) and 286 (36,200). This solution is moderately stable in the dark, but undergoes a facile photolysis. The irradiation was restricted to wavelengths above 325 nm in order to prevent light absorption by and subsequent photoreactions of the solvent [12]. The photolysis is accompanied by spectral changes (Fig. 1). They clearly indicate the formation of $Fe^{III}(et_2dtc)_2Cl$, which absorbs at $\lambda_{max} = 625$ nm (3600), 442 (7400), 371 (6500), 310 (18,500) and 251 (39,700). At the isosbestic points, $Fe^{II}(et_2dtc)_2(CO)_2$ and $Fe^{III}(et_2dtc)_2Cl$ have the same extinction coefficients: $\lambda = 386$ nm (4800), 345 (7200), 307 (16,600) and 272 (27,500). The isosbestic points are preserved over extended irradiation times. The photolysis can be driven almost to completion without a serious interference by secondary photoreactions. The progress of the photolysis was monitored by measuring the increase of the absorbance at 625 nm. The photoproduct $Fe^{III}(et_2dtc)_2Cl$ was formed with $\phi = 0.0015$ at $\lambda_{irr} = 366$ nm.

4. Discussion

The complex $Fe^{II}(et_2dtc)_2(CO)_2$ is diamagnetic and has a singlet ground state [8]. Low-energy electronic transitions are expected to be of the ligand-field (LF) and metal-to-ligand charge transfer (MLCT) type [14], while ligand-to-metal charge transfer (LMCT) transitions should not occur at low energies in agreement with the redox properties of low-spin Fe(II) complexes. The 286 nm absorption of $Fe^{II}(et_2dtc)_2(CO)_2$ is assigned to a $\pi\pi^*$ intraligand (IL) transition, which appears in the same energy region for the free et_2dtc^- ligand [15]. The 360 nm band of the complex is assigned to a $Fe^{II} \rightarrow \pi^*$ (et_2dtc^-) MLCT transition. Owing to the intensity of this band ($\varepsilon = 8600$), an LF assignment is not appropriate although an LF absorption of much lower intensity may be present at comparable energies. A distinct charge-transfer-to-solvent (CTTS) absorption, as occurs for ferrocene in halocarbon solvents [16–18], does not appear in the spectrum of $Fe^{II}(et_2dtc)_2(CO)_2$ in $CHCl_3$, as indicated by the observation that the spectra in $CHCl_3$ and CH_3CN are quite similar.

The photolysis of $Fe^{II}(et_2dtc)_2(CO)_2$ in $CHCl_3$ proceeds according to a simple equation:

$$Fe^{II}(et_2dtc)_2(CO)_2 + CHCl_3 \rightarrow Fe^{III}(et_2dtc)_2Cl + 2CO + CHCl_2\text{-radical} \quad (1)$$

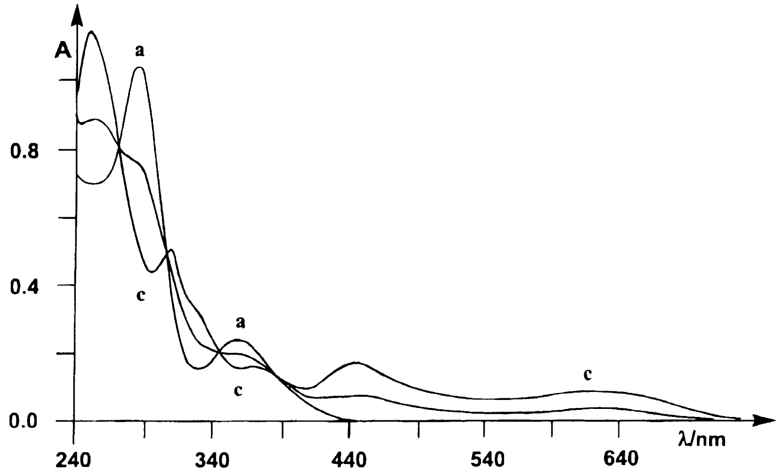

Fig. 1. Spectral changes during the photolysis of 3.89×10^{-5} M $Fe^{II}(et_2dtc)_2(CO)_2$ in $CHCl_3$ under argon at room temperature after 0 min (a), 5 and 10 min (c) irradiation times with $\lambda_{irr} > 325$ nm (Osram HBO 200 W/2 lamp; Schott cut-off WG 345), 1 cm cell.

A variety of reducing complexes have been shown to be photooxidized by chlorinated alkanes in a similar fashion [11,12,18]. The solvent radical derived from the solvent participates in various secondary reactions. In analogy to other photooxidations of this type, the photolysis ($\lambda_{irr} = 366$ nm) of $Fe^{II}(et_2dtc)_2(CO)_2$ apparently originates from an MLCT state, which facilitates a subsequent electron transfer to the solvent [11]. The release of CO is certainly associated with the lack of stability of Fe(III) carbonyl complexes (e.g. $[Fe^{III}(CN)_5(CO)]^{2-}$) [19]. However, it must be admitted that the photooxidation could also start from an LF state which may be populated from the MLCT state. An LF state is expected to induce the release of CO, as occurs in the case of $[Fe^{II}(CN)_5(CO)]^{3-}$ [20–22]. As a result, a strongly reducing and coordinatively unsaturated $Fe^{II}(et_2dtc)_2$ fragment might be generated and thermally oxidized by $CHCl_3$ to yield $Fe^{III}(et_2dtc)_2Cl$.

At this point it should be mentioned that $Fe^{III}(R_2dtc)_2Cl$, with R = ethyl and benzyl, is also formed upon irradiation of $Fe^{III}(R_2dtc)_3$ in chlorinated alkanes [23–28]:

$$Fe^{III}(R_2dtc)_3 + R'\text{–}Cl \xrightarrow{h\nu} Fe^{III}(R_2dtc)_2Cl + R_2dtc\text{-}R' \qquad (2)$$

In this case the photolysis is induced by LMCT excitation, which generates Fe(II) in the primary photochemical step:

$$Fe^{III}(R_2dtc)_3 \xrightarrow{h\nu} Fe^{II}(R_2dtc)_2 + R_2dtc\text{-radical} \qquad (3)$$

Product formation then takes place by a solvent-initiated reoxidation of Fe(II). As an overall result, the oxidation state Fe(III) is preserved but a dtc^- ligand is finally oxidized. Quite recently, we have shown that the primary product of this photoreduction, $Fe^{II}(R_2dtc)_2$ with R = ethyl, is intercepted and stabilized by 1,2-bis(diphenylphosphino)ethane (dppe) [29]:

$$Fe^{III}(et_2dtc)_3 + dppe \xrightarrow{h\nu} Fe^{II}(et_2dtc)_2(dppe) + \tfrac{1}{2}(et_2dtc)_2 \qquad (4)$$

This observation and the results of the present work show that dithiocarbamato complexes of iron(II) and iron(III) can be photooxidized by MLCT excitation and reduced by LMCT excitation, respectively. Other iron complexes with sulfur ligands, particularly compounds with biological significance, may undergo similar photoredox processes which lead to reversible changes between Fe(II) and Fe(III). In this context it is of interest that iron sulfides have been suggested to play an important role as catalysts for the evolution of early life on Earth [30–32]. As a speculative idea it might be added that such processes could also proceed as light-induced reactions with iron sulfides as photoredox catalysts.

Acknowledgements

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