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Preliminary communication

Photoreactivity of $Fe_2S_2(CO)_6$ originating from dσ^* metal-to-ligand charge transfer excitation

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Abstract

The longest-wavelength absorption of $Fe_2S_2(CO)_6$ near 460 nm is assigned to a metal-to-ligand charge transfer (MLCT) transition from the Fe–Fe bond to a S–S antibonding orbital. It is suggested that MLCT excitation leads to an oxidative addition. The primary photoproduct reacts with $Fe_2S_2(CO)_6$ to generate $Fe_4S_4(CO)_{12}$. This well known photodimerization proceeds with $\phi = 0.045$ at $\lambda_{irr} = 436$ nm. © 1998 Elsevier Science S.A. All rights reserved.

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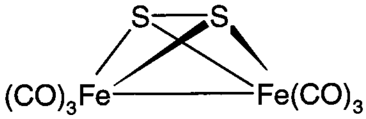
1. Introduction

Iron–sulfur compounds in general, and clusters in particular, play an important role in chemistry and biology. As metallo enzymes they participate in biochemical redox processes such as photosynthesis and nitrogen fixation. In recent years much work has been carried out in order to elucidate the electronic structure of iron–sulfur clusters [1–4]. Surprisingly, very little is known about the nature and reactivity of electronically excited states of these compounds [5]. We considered this possibility and selected the complex $Fe_2S_2(CO)_6$ for the present study.



This cluster is well characterized [6–8] and thermally quite stable below 50°C. However, $Fe_2S_2(CO)_6$ is light-sensitive and undergoes a variety of photoreactions such as dimerization [8] and addition to carbon–carbon double bonds [9–13]. Unfortunately, these investigations were limited to applications in synthesis, while the electronic spectra and their significance for the photoreactivity have not yet been explored.

2. Results

The electronic spectrum of $Fe_2S_2(CO)_6$ in CH_3CN (Fig. 1) shows absorptions at $\lambda_{max} = 449$ ($\varepsilon = 1080$ M^{-1} cm^{-1}), 336 (11200), 278 (8300) and 218 nm (27600). The complex is slightly solvatochromic. The longest-wavelength band undergoes a moderate red shift with decreasing solvent polarity: $\lambda_{max} = 457$ nm ($CHCl_3$) and 464 nm (hexane). The light sensitivity of $Fe_2S_2(CO)_6$ has been reported previously [9–13]. In the absence of suitable scavengers, a photodimerization takes place [8]. At higher concentrations $Fe_4S_4(CO)_{12}$ precipitates owing to its small solubility [8,14]. At lower concentrations ($< 10^{-4}$ M) the formation of the tetramer can be followed by spectrophotometry (Fig. 1). The concomitant spectral changes include isosbestic points at 356,

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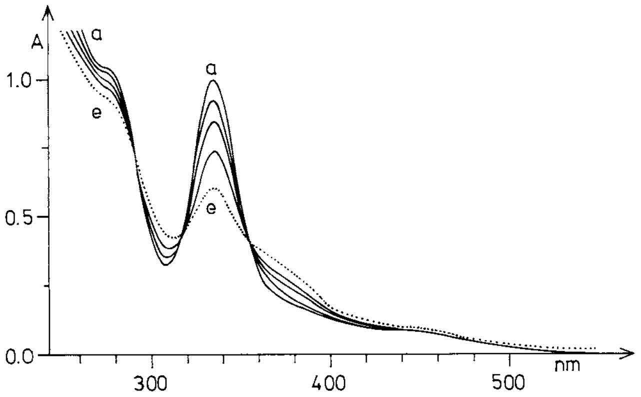

Fig. 1. Spectral changes during the photolysis of 8.9 × 10^{-5} M $Fe_2S_2(CO)_6$ in CH_3CN under argon at r.t. after (a) 0, 1, 2, 4 and (e, ...) 7 min irradiation times, with $\lambda_{irr} = 436$ nm (Xe/Hg 977 B-1, 1kW lamp), 1 cm cell.

317 and 291 nm during early stages of the photolysis indicating a rather clean reaction. The photodimerization is monitored by measuring the decrease of the optical density at 336 nm. At this wavelength the extinction coefficients are $\varepsilon = 11200$ for $Fe_2S_2(CO)_6$ and 3200 for $Fe_4S_4(CO)_{12}$. The quantum yield of dimerization is $\phi = 0.045$ at $\lambda_{irr} = 436$ nm.

At later stages of the photolysis of $Fe_2S_2(CO)_6$ a secondary photoreaction takes place. It is associated with the photodecomposition of $Fe_4S_4(CO)_{12}$. The accompanying spectral variations (Fig. 2) terminate at a final absorption which extends over the entire wavelength range and increases towards shorter wavelength. This featureless spectrum is apparently caused by a colloid which finally yields a precipitate. This solid is simply FeS. An authentic sample of FeS is characterized by the same FTIR spectrum as that of the photoproduct. Moreover, the IR spectrum of the photoproduct does not contain typical absorptions of CO stretching vibrations around 2000 cm^{-1}, indicating the absence of CO ligands.

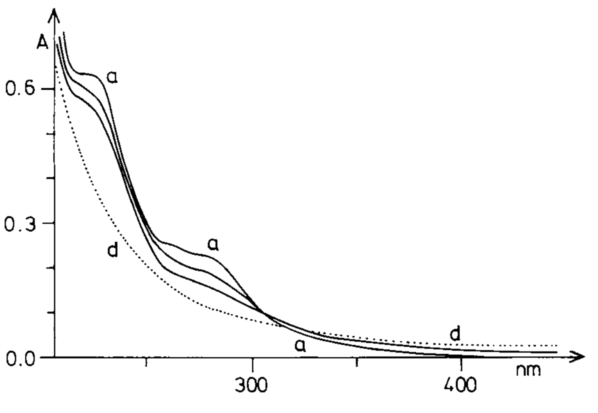

Fig. 2. Spectral changes during the photolysis of 1.63 × 10^{-5} M $Fe_4S_4(CO)_{12}$ in CH_3CN under argon at r.t. after (a) 0, 2, 4 and (d, ...) 20 min irradiation times, with white light (HBO 100 W/2 lamp), 1 cm cell.

3. Discussion

On the basis of structural data [7] and MO calculations [15], $Fe_2S_2(CO)_6$ can be roughly described as a complex with a bridging disulfide ligand and a metal–metal bond which connects two Fe(I) d^7-centers. The HOMO ($15a_1$) is represented by the Fe–Fe σ-bond while the LUMO ($10b_1$) is antibonding with regard to the S–S bond. The lowest-energy transition from the HOMO to the LUMO is thus of the metal-to-ligand charge transfer (MLCT) type and involves the promotion of an electron from the Fe–Fe bond into the S–S antibonding orbital. Although the LUMO is composed of π^* (S–S) as well as σ^* (S–S) orbitals the antibonding nature is dominated by the σ^* contribution. Accordingly, the MLCT transition is of the $d \rightarrow \sigma^*$ type. The longest-wavelength absorption of $Fe_2S_2(CO)_6$ near 460 nm is then logically assigned to this $d\sigma^*$ MLCT transition. This assignment is corroborated by the solvent dependence of the MLCT absorption [16]. The negative solvatochromism of $Fe_2S_2(CO)_6$ is consistent with this assignment. In this context it is quite interesting that the electronic structure and spectrum of $Fe_2S_2(CO)_6$ are related to those of $Re_2Br_2(Se_2Ph_2)(CO)_6$ [17]. In the latter case a metal–metal bond does not exist. However, the lowest-energy transition is also of the $d\sigma^*$ MLCT type. It involves the promotion of an electron from the Re(I) d^6-center to the σ^* orbital of the bridging diselenide ligand.

Generally, $d\sigma^*$ MLCT excitation favors oxidative additions [18]. Since the MLCT transition of $Fe_2S_2(CO)_6$ is associated with the shift of electron density from the Fe^I–Fe^I bond to the disulfide bridge, the primary photochemical step may lead to the generation of two $Fe^{II}(S^{2-})(CO)_3$ fragments. These could still exist as a loosely bonded dimer via sulfide or carbonyl bridges in order to achieve octahedral coordination for the Fe(II) d^6-centers. $Fe^{II}(S^{2-})(CO)_3$ or its dimer is certainly reactive enough to add to an intact ground state dimer:

$$Fe^I_2(S_2^{2-})(CO)_6 \quad \text{—}\mathbf{MLCT}\rightarrow$$

$$2Fe^{II}(S^{2-})(CO_3) \text{ or } [Fe^{II}(S^{2-})(CO)_3]_2$$

$$2Fe(S)(CO)_3 + Fe_2S_2(CO)_6 \rightarrow Fe_4S_4(CO)_{12}$$

Product formation does not only occur by the formation of the tetramer, but also by the addition of other suitable substrates such as olefins [10–12] and fullerene [13].It is quite intriguing that the tetramer is also light-sensitive and loses simply CO with the concomitant formation of FeS. Since photoreactions can be controled much better than thermal reactions, the photolysis of $Fe_4S_4(CO)_{12}$ may be utilized to generate FeS with desired properties such as a certain particle size or size distribution. Applications in nanotechnology are thus feasible.

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