Photoreactivity of Titanocene Pentasulfide
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The electronic spectrum of Cp₂TiS₅ shows a long-wavelength absorption at λₘₐₓ = 492 nm which is assigned to the lowest-energy S₅⁺−TiIV ligand-to-metal charge transfer (LMCT) transition. The photolysis of the complex in CH₂Cl₂ leads to the formation of Cp₂TiCl₂ and elemental sulfur. It is suggested that LMCT excitation initiates a reductive elimination with the extrusion of S₅ while the reduced titanocene is reoxidized by the solvent.

1. Introduction
The electronic spectra and photochemistry of transition metal complexes which contain sulfur-coordinating ligands have been studied extensively for many years. Very simple compounds of this type are the tetrasulfido complexes of the d⁰ metal ions such as V⁵⁺, Mo⁶⁺, W⁶⁺ and Re⁷⁺ [1, 2]. Their absorption spectra are characterized by low-energy ligand-to-metal charge transfer (LMCT) bands. LMCT excitation induces photoredox processes [3]. In contrast to these thiometallates very little is known about the electronic spectra and photoreactivity of polysulfide complexes which contain S₅²− (x > 1) ligands although the general chemistry of such compounds has attracted much attention [4]. This class of coordination compounds includes complexes such as [PtIV(S₅)]₂− and Cp₂TiIVS₅ which contain penta sulfide, S₅²−, as a bidentate ligand. In order to explore the electronic spectra and photoreactivity of compounds with MS₅ moieties we selected Cp₂TiIVS₅ for the present study. This choice is based on several considerations. The photochemistry of a variety of titanocene derivatives has been studied in quite some detail [5,6]. The spectra of simple Cp₂TiX₂ complexes show only LMCT absorptions [5, 7]. These observations should facilitate the present investigation. In this context it is quite surprising that the photochemical formation but not the light sensitivity of Cp₂TiS₅ were reported 20 years ago [8].

2. Experimental
2.1. Materials
Cp₂TiS₅ was commercially available by Aldrich. All solvents were spectrograde.

2.2. Photolyses
The light source was an Osram HBO 100 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using a Schoeffel GM 250/1 high-intensity monochromator (band width 20 nm). The photolyses were carried out in solutions of CH₂Cl₂, CHCl₃, and CH₃CN in 1 cm spectrophotometer cells at room temperature. Solutions were air saturated since deaeration did not affect the results. Progress of the photolyses was monitored by UV-visible spectrophotometry. The photoproducts were identified by their absorption spectra. 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 a Packard 8452A diode array or an Uvikon 860 absorption spectrometer.

2.3. Instrumentation
Absorption spectra were measured with a Hewlett Packard 8452A diode array or an Uvikon 860 absorption spectrometer.

3. Results
The electronic spectrum of Cp₂TiS₅ in CH₂Cl₂ (Fig. 1) shows absorptions at λₘₐₓ = 492 (ε = 2300 M⁻¹ cm⁻¹), 376 (sh, 2400), 316 (11800), and 288 (sh, 10100) nm. This solution is light sensitive. The photolysis of Cp₂TiS₅ in CH₂Cl₂ is associated with spectral variations (Fig. 1) which...
Fig. 1. Spectral changes during the photolysis of $1.68 \times 10^{-4}$ M Cp$_2$TiS$_5$ in CH$_2$Cl$_2$ after 0 (a), 2, 4 and 6 (d) min irradiation time with $\lambda_{irr} = 366$ nm, 1-cm cell.

include isosbestic points at $\lambda = 432$, 380 and 287 nm. The spectral changes are indicative of the formation of Cp$_2$TiCl$_2$ which displays absorptions at $\lambda_{max} = 522$ ($\varepsilon = 240$), 393 (2400) and 312 (5800) nm [9,10]. The formation of Cp$_2$TiCl$_2$ is also confirmed by its reaction with [Ru(CN)$_6$]$^{4-}$ which generates the trinuclear complex ion {Cp$_2$Ti$^{IV}$[µ-NCRu$^{II}$(CN)$_5$]$_2$}$_6^{-}$ ($\lambda_{max} = 630$ nm) [6]. However, the spectral changes (Fig. 1) could not be simulated assuming that Cp$_2$TiCl$_2$ is the only compound which is formed during the photolysis. Another photoproduct is characterized by an absorption which extends from the visible to the UV and increases in intensity towards shorter wavelength. This apparent absorption is obviously caused by colloidal particles which scatter the light. At higher concentrations of Cp$_2$TiS$_5$ ($\sim 10^{-2}$ M) the colloid in the photolyzed solution becomes visible in a Tyndall effect. The colloid which can be removed by centrifuging the photolyzed solution consists of elemental sulfur. It is identified by its absorption spectrum at $\lambda_{max} = 278$ and 266 nm in cyclohexane [11]. The photolysis is not influenced by the presence of oxygen. Irradiation of argon-saturated solutions leads to the same results. The progress of the photolysis is monitored by measuring the decrease of absorbance at $\lambda = 492$ nm. The efficiency of the photoreaction depends on the wavelength of irradiation. Quantum yields are $\phi = 0.02$ at $\lambda_{irr} = 366$ nm and 0.005 at $\lambda_{irr} = 436$ nm.

4. Discussion

The electronic structures and spectra of various titanocene derivates with the general formula Cp$_2$TiX$_2$ have been studied in detail. All low-energy transitions of these pseudo-tetrahedral complexes are of the LMCT type and involve the promotion of an electron from the Cp$^-$ or X$^-$ ligands to the d$^8$ metal center [5, 7, 9, 10]. If X$^-$ is rather reducing (e.g. X = Br, alkyl, aryl) the longest-wavelength absorptions are assigned to X$^- \rightarrow$ Ti$^{IV}$ LMCT transitions. Cp$_2$TiS$_5$ belongs to the C$_s$ symmetry class and all MOs are of the a’ and a” type [12]. Since all transitions between these orbitals are allowed [13] the absorptions of Cp$_2$TiS$_5$ are rather intense (Fig. 1). By comparison with the spectra of other titanocene derivates [5, 7, 9, 10] and in agreement with previous calculations [12] the longest-wavelength band of Cp$_2$TiS$_5$ at $\lambda_{max} = 492$ nm is assigned to the lowest-energy S$_5^{2-} \rightarrow$ Ti$^{IV}$ LMCT transition. The bands at shorter wavelengths are also of the S$_5^{2-} \rightarrow$ Ti$^{IV}$ LMCT type, but Cp$^-$ $\rightarrow$ Ti$^{IV}$ LMCT absorptions may occur in the same energy region.

The photolysis of Cp$_2$TiS$_5$ in CH$_2$Cl$_2$ leads to the formation of Cp$_2$TiCl$_2$ and elemental sulfur. This observation can be rationalized on the basis of a reactive S$_5^{2-} \rightarrow$ Ti$^{IV}$ LMCT state. LMCT excitation is followed by a two-electron reductive elimination at Ti$^{IV}$ with concomitant extrusion of S$_5$ which is finally converted to S$_8$ as the stable form of elemental sulfur. This reductive elimination can proceed as a concerted process or in two consecutive one-electron transfer steps. In the absence of a suitable scavenger a recombination of the starting complex occurs in analogy to its photochemical formation [8]. However, chlorinated alkanes are well known to function as efficient oxidants in photoredox reactions of transition metal complexes [5, 14]. This reaction competes successfully with the recombination. The reduction of R-Cl leads to the release of chloride which is available for coordination at the metal atom while the radical R undergoes secondary reactions. The overall photolysis of Cp$_2$TiS$_5$ can then be rationalized by the following equation:

$$\text{Cp}_2\text{Ti}^{IV}\text{S}_5 + 2 \text{CH}_2\text{Cl}_2 \xrightarrow{\text{hv}} \text{Cp}_2\text{Ti}^{IV}\text{Cl}_2 + \text{S}_8 + 2 \text{CH}_2\text{Cl}$$

In this context it is quite interesting that the photoreduction of some other titanocene derivates in chlorocarbons is also associated with the re-oxidation by the solvent [6,9,10]. In the case of Cp$_2$Ti$^{IV}$[µ-NCRu$^{II}$(CN)$_5$]$_2$ MMCT excitation leads to a one-electron reduction of Ti$^{IV}$ to yield Cp$_2$Ti$^{II}$[µ-NCRu$^{II}$(CN)$_5$]$_3^{-}$ which is scavenged by CHCl$_3$ and finally converted to Cp$_2$Ti$^{IV}$Cl[µ-NCRu$^{II}$(CN)$_5$]$_3^{-}$ [6]. The photolysis of Cp$_2$TiMe$_2$
produces several products including \( \text{Cp}_2\text{Ti(Me)Cl} \) and \( \text{Cp}_2\text{TiCl}_2 \) \[9\]. It seems that these photoreactions involve competing one- and two-electron reductions of \( \text{Ti}^{IV} \) with subsequent reoxidation by \( \text{CHCl}_3 \).

The quantum yield of the photolysis of \( \text{Cp}_2\text{TiS}_5 \) is dependent on the wavelength of irradiation. Although an obvious explanation is not available presently it is feasible that higher-energy \( \text{S}_5^{2-} \to \text{Ti}^{IV} \) LMCT excited states are more reactive. In the case of \( \text{MS}_4^{n-} \) with \( \text{M} = \text{V}^{V}, \text{Mo}^{VI}, \text{W}^{VI} \) and \( \text{Re}^{VII} \) an analogous behavior has been observed \[3\].

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