

# Photodisproportionation of (1,5-Cyclooctadiene)copper(I) Hexafluoroacetylacetonate Induced by Metal-to-Ligand Charge Transfer Excitation

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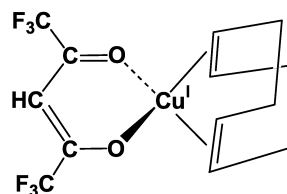
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The complex  $\text{Cu}^{\text{I}}(\text{COD})(\text{hfac})$  with COD = 1,5-cyclooctadiene and hfac = hexafluoroacetylacetonate shows two long-wavelength absorptions at  $\lambda_{\text{max}} = 308$  and 241 nm which are assigned to hfac intraligand (IL) and  $\text{Cu}^{\text{I}} \rightarrow \text{COD}$  metal-to-ligand charge transfer (MLCT) transitions, respectively. The photolysis of  $\text{Cu}^{\text{I}}(\text{COD})(\text{hfac})$  in hexane leads to the release of the olefin and the subsequent disproportionation of  $\text{Cu}^{\text{I}}(\text{hfac})$  to elemental copper and  $\text{Cu}^{\text{II}}(\text{hfac})_2$  with the quantum yields  $\phi = 10^{-3}$  at  $\lambda_{\text{irr}} = 313$  nm and  $\phi = 3 \times 10^{-3}$  at  $\lambda_{\text{irr}} = 254$  nm. It is suggested that the reactive excited state is of the MLCT type.

**Key words:** Electronic Spectra, Photochemistry, Copper Complexes, Olefin Complexes

## Introduction

The photochemistry of olefin complexes of transition metals has been studied in quite some detail [1,2]. In particular, copper(I) olefin complexes have been shown to undergo a variety of photoreactions [1,3–5]. Frequently, the irradiation is followed by transformations of the olefin. Unfortunately, in most cases the nature of the photoactive compound was not clear since metal complexes as well as free olefins were present as light-absorbing species. Accordingly, the role of copper(I) is not well defined. We suspected that in the primary photoreaction copper(I) olefin complexes might simply release the olefin in analogy to some olefin complexes of other  $d^{10}$  metals [1,2] such as Pt(0) [6,7]. We explored this possibility and selected the compound  $\text{Cu}(\text{COD})(\text{hfac})$  with COD = 1,5-cyclooctadiene and hfac = hexafluoroacetylaceto-



nate for the present study. This choice was guided by the following considerations.  $\text{Cu}(\text{COD})(\text{hfac})$  is easily accessible [8] and commercially available (Alfa Aesar). Cu(I) olefin complexes are characterized by low-energy metal-to-ligand charge transfer (MLCT) excited states [9]. Since metal-olefin complexes are stabilized by  $\pi$ -acceptor bonding, MLCT excitation leads to a considerable weakening of the metal-olefin bond which, in turn, can induce the release of the olefin. If this happens in the case of  $\text{Cu}(\text{COD})(\text{hfac})$  the photolysis yields  $\text{Cu}(\text{hfac})$ . In the absence of a coordinating solvent  $\text{Cu}(\text{hfac})$  is not stable but disproportionates to metallic copper and  $\text{Cu}^{\text{II}}(\text{hfac})_2$  [10]. This disproportionation can be used as a probe for the photochemical release of the olefin. Moreover, the photochemical deposition of metallic copper is quite interesting in its own right. In this context it is rather important that complexes of the type  $\text{CuL}(\text{hfac})$  including  $\text{Cu}(\text{COD})(\text{hfac})$  are useful precursors for the chemical vapor deposition of metallic copper [8,11,12]. In this case these compounds lose L thermally at higher temperatures.

## Experimental Section

### Materials

All solvents used for spectroscopic measurements were of spectrograde quality.  $\text{Cu}(\text{COD})(\text{hfac})$  was commercially available (Alfa Aesar) and used without further purification.

### Instrumentation

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 spectrophotometer. Emission spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations. 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-

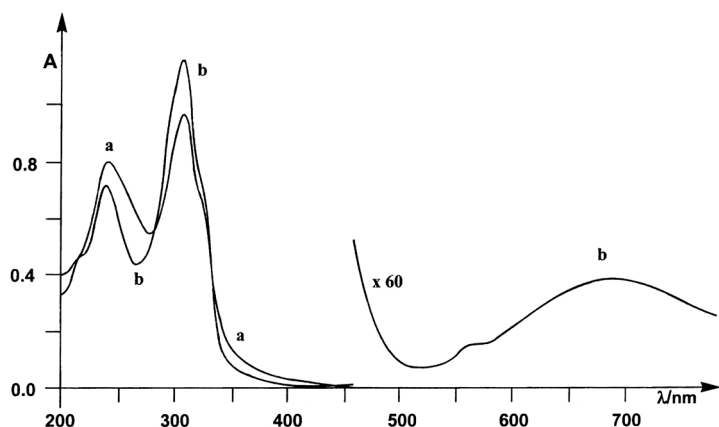


Fig. 1. Spectral changes during the photolysis of  $6.65 \times 10^{-4}$  M Cu(COD)(hfac) in *n*-hexane under argon at r.t. after 0 min (a) and 12 min (b) irradiation times with white light (Osram HBO 200 W/2 lamp), 1-mm cell.

intensity monochromator (band width 23 nm) with additional Schott cutoff filters to avoid short-wavelength and second order irradiation. In all cases the light beam was focused on a thermostated photolysis cell by a quartz lens.

#### Photolyses

The photolyses were carried out in solutions of *n*-hexane in 1 or 0.1 cm spectrophotometer cells at room temperature under argon. Progress of the photolyses was monitored by UV-visible 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 an RkP-345 detector.

#### Results

Since Cu(COD)(hfac) is slowly oxidized by oxygen all solutions were saturated with argon. The electronic spectrum of Cu(COD)(hfac) in *n*-hexane (Fig. 1) displays absorptions at  $\lambda_{\max} = 326$  nm (sh,  $\epsilon = 10300 \text{ M}^{-1} \text{ cm}^{-1}$ ), 308 (14800) and 241 (12300). In acetonitrile at low concentrations as used for spectral measurements the COD ligand is completely displaced by the solvent. The absorption spectrum of the resulting Cu(CH<sub>3</sub>CN)<sub>n</sub>(hfac) (Fig. 2) has lost all bands which can be attributed to the presence of the COD ligand (see discussion). Above 230 nm the spectrum contains only the absorptions of the coordinated hfac ligand [13] at 312 (sh, 11500) and 304 nm (13200). Cu(COD)(hfac) does not show any luminescence at r. t.

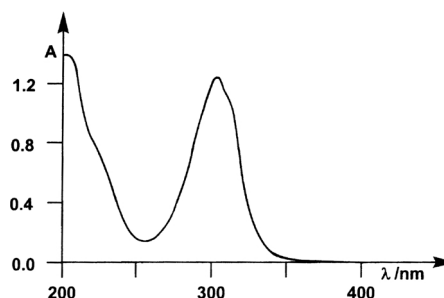


Fig. 2. Electronic absorption spectrum of  $1.09 \times 10^{-4}$  M Cu(COD)(hfac) in CH<sub>3</sub>CN under argon at r. t., 1-cm cell.

or 77 K. At r. t. in *n*-hexane Cu(COD)(hfac) undergoes a thermal reaction which is accelerated upon irradiation. The accompanying spectral changes (Fig. 1) indicate the formation of Cu<sup>II</sup>(hfac)<sub>2</sub> which shows a diagnostic band at  $\lambda_{\max} = 690$  nm ( $\epsilon \sim 80$ ) [14]. Moreover, elemental copper is formed as a colloid. The colloidal particles exhibit an apparent absorption spectrum which covers the whole visible and UV region with an increasing extinction towards shorter wavelength. This type of spectrum which is simply caused by light scattering is generally observed for copper colloids [15–17]. Moreover, a small inflection at 560 nm (Fig. 1) is indicative of a plasmon absorption of colloidal copper. The metallic copper can be separated by centrifugation. It dissolves in nitric acid. Upon dilution and addition of ammonia the blue complex [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ( $\lambda_{\max} = 616$  nm) is formed. The progress of the photolysis was monitored by measuring the increase of the absorption of Cu<sup>II</sup>(hfac)<sub>2</sub> at 690 nm. Owing to the interference by the thermal reaction and light scattering by metallic copper the quantum yields of the photolysis could only be estimated. They are ap-

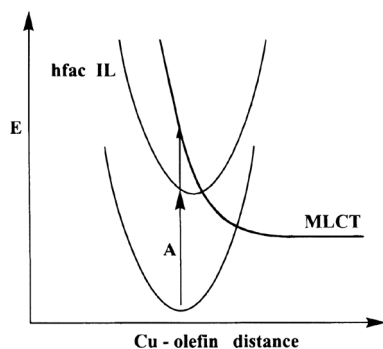


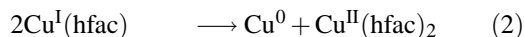
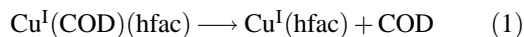
Fig. 3. Potential energy diagram for the ground and lowest-energy excited states of  $\text{Cu}(\text{COD})(\text{hfac})$ .

proximately  $\phi = 0.001$  at  $\lambda_{\text{irr}} = 313$  nm and  $\phi = 0.003$  at  $\lambda_{\text{irr}} = 254$  nm.

### Discussion

Owing to its importance for chemical vapor deposition the complex  $\text{Cu}(\text{COD})(\text{hfac})$  has been investigated in great detail [11,18–21]. However, previous studies did not include the examination of the electronic spectra and photochemistry. The absorption spectrum of the complex in *n*-hexane (Fig. 1) contains two bands which are attributed to hfac intraligand (IL) ( $\lambda_{\text{max}} = 308$  nm) and  $\text{Cu}^{\text{I}} \rightarrow \text{COD}$  metal- to-ligand charge transfer (MLCT) ( $\lambda_{\text{max}} = 241$  nm) transitions. These assignments are based on the following considerations. The 308 nm absorption including its long-wavelength shoulder ( $\sim 326$  nm) indicates the presence of the coordinated hfac ligand [13]. Generally,  $\text{Cu}(\text{I})$  olefin complexes are characterized by UV absorptions below 280 nm [1, 3]. These bands were suggested to be of the ligand-to-metal charge transfer (LMCT) or MLCT type. However, recent calculations have shown that these transitions are definitely MLCT in nature [9]. In acetonitrile the olefin ligand of  $\text{Cu}(\text{COD})(\text{hfac})$  is apparently substituted and  $\text{Cu}(\text{CH}_3\text{CN})_n(\text{hfac})$  is formed as indicated by the absence of the  $\text{Cu}^{\text{I}} \rightarrow \text{COD}$  MLCT absorptions. Although this observation is new the lability of the COD ligand has been previously noticed

[11, 19]. In hexane solutions  $\text{Cu}(\text{COD})(\text{hfac})$  is more stable owing to the absence of a coordinating solvent but a slow displacement of COD takes also place in this solvent. This dissociation is followed by the well-known disproportionation of  $\text{Cu}(\text{hfac})$  [10]:



These processes occur also during the chemical vapor deposition of copper. Solid  $\text{Cu}(\text{COD})(\text{hfac})$  reacts according to this scheme at 200 °C [11].

Since the lowest-energy absorption of  $\text{Cu}(\text{COD})(\text{hfac})$  at  $\lambda_{\text{max}} = 308$  nm belongs to a hfac IL transition it may be suspected that this IL state determines the excited state behavior of the complex. In this case, however, a structured IL phosphorescence near 500 nm should appear [13,22,23]. In contrast to this expectation  $\text{Cu}(\text{COD})(\text{hfac})$  does not emit but is light-sensitive. We suggest that the photochemical release of the COD ligand is initiated by  $\text{Cu}^{\text{I}} \rightarrow \pi^*$  (COD) MLCT excitation. Owing to the great importance of  $\pi$ -bonding in metal-olefin complexes the population of a  $\text{Cu}$ -olefin  $\pi^*$  orbital is associated with a considerable weakening of the  $\text{Cu}$ -olefin bond which finally leads to the dissociative loss of the olefin and the subsequent disproportionation of  $\text{Cu}(\text{hfac})$ . The relationship between hfac IL and MLCT state is shown in Fig. 3. In absorption the IL state is located below the MLCT state which however extends to lower energies along the dissociation path. Direct IL excitation is largely followed by the population of the reactive MLCT state.

In conclusion, the complex  $\text{Cu}(\text{COD})(\text{hfac})$  in hexane undergoes a thermal and photochemical release of COD. A subsequent disproportionation of  $\text{Cu}(\text{hfac})$  leads to the formation of elemental copper and  $\text{Cu}^{\text{II}}(\text{hfac})_2$ . The photolysis is induced by  $\text{Cu}^{\text{I}} \rightarrow \pi^*$  (COD) MLCT excitation.

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