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Photochemistry of cyclopentadienylthallium(I) *

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Abstract

TlC₅H₅ displays absorption maxima at 228 and 280 nm which are assigned to metal-centred sp and ligand-to-metal charge transfer (LMCT) transitions, respectively. The complex shows an emission at $\lambda_{\text{max}} = 360$ nm which originates from a low-energy sp excited state. The photolysis of TlC₅H₅ in methanol proceeds according to the equation $\text{TlC}_5\text{H}_5 + \text{CH}_3\text{OH} \rightarrow \text{TlOH} + \text{H}_2 + \text{C}_6\text{H}_6$ (pentafulvene) with $\phi = 0.1$ at $\lambda_{\text{irr}} = 254$ nm and 0.008 at 313 nm. It is suggested that this photoreaction is induced by LMCT excitation.

1. Introduction

While the photochemistry of transition metal complexes with aromatic ligands such as benzene or the cyclopentadienyl anion (C₅H₅⁻ = Cp⁻) has been studied extensively for many years [1,2] light-induced processes of organometallic compounds of main group metals with such ligands have been completely ignored. A few years ago we started a systematic investigation of the photochemistry of main group metal complexes in general [3–5]. In the meantime we revealed some important features of the excited states of main group metal complexes with simple ligands such as chloride. The present study proceeds one step further and combines the photochemistry of coordination compounds of the main group metals and organometallics with aromatic ligands which utilize their π -electrons for metal–ligand bonding. This photochemistry should not only be interesting in its own right but may also lead to important applications such as C–C or C–H bond activation. In this context it is quite intriguing that atomic mercury which has the same electronic structure as Tl⁺ photosensitizes the dehydrodimerization of organic compounds in solution [6,7] and in the gas phase [8].

Suitable candidates for the present study are cyclopentadienyl [9] or benzene [10] complexes of s² metals such as Ga⁺, In⁺, Tl⁺, Ge²⁺, Sn²⁺, Pb²⁺, Sb³⁺ or Bi³⁺. We selected the complex TlCp which had first been prepared by Fischer in 1957 [11,12]. This compound offers several advantages. It is easily prepared [13] or commercially available. Moreover, TlCp is surprisingly stable toward hydrolysis and oxidation by oxygen. Owing to these properties TlCp has been used extensively as a versatile reagent in organometallic synthesis [13].

2. Experimental details

TlC₅H₅ was purchased from Aldrich and purified by sublimation. Methanol was spectrograde.

The light source was a Hanovia Xe/Hg 977 B-1 (1000 W) lamp. Monochromatic light ($\lambda_{\text{irr}} = 254$ and 313 nm) was obtained by means of a Schoeffel GM 250-1 high-intensity monochromator. The photolyses were carried out at room temperature in 1 cm spectrophotometer cells. 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 and equipped with a RkP-345 detector.

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* Dedicated to Prof. Dr. Dr. h. c. mult. Ernst Otto Fischer, on the occasion of his 75th birthday.

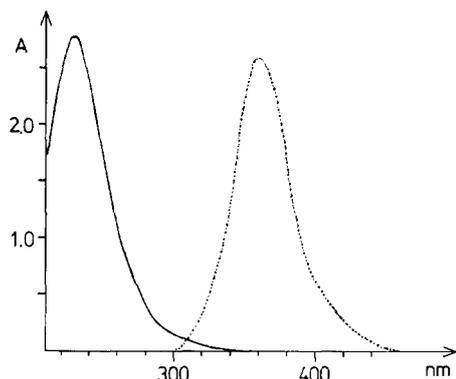


Fig. 1. Electronic absorption (left side) and emission (right side) spectra of TlC_5H_5 in methanol at room temperature, 1 cm cell. Absorption: 3.57×10^{-4} M. Emission: 1.78×10^{-4} M, $\lambda_{\text{exc}} = 250$ nm, intensity in arbitrary units.

Progress of photolysis was monitored by UV-visible spectrophotometry, using a 8452 Hewlett Packard diode array spectrophotometer.

3. Results

TlCp is moderately soluble in polar organic solvents. For spectroscopic and photochemical studies methanol is a suitable solvent since it is transparent in the UV region. The electronic spectrum of TlCp (Fig. 1) consists of an absorption maximum at $\lambda = 228$ nm ($\epsilon = 7800 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at $\lambda \text{ ca. } 280$ nm ($\epsilon = 1100$). Solutions of TlCp in methanol were also emissive. A luminescence appeared at $\lambda_{\text{max}} = 360$ nm (Fig. 1) with a quantum yield of approximately 10^{-3} . The excitation spectrum agreed well with the absorption spectrum including the long-wavelength shoulder.

Upon irradiation of TlCp in CH_3OH photolysis took place which led to the release of hydroxide as indicated by an increase of the pH. In addition hydrogen was detected by gas chromatography. The photolysis was accompanied by spectral variations (Fig. 2) which gave clear evidence for the formation of pentafulvene C_6H_6 ($\lambda_{\text{max}} = 362$ nm, $\epsilon = 230$; $\lambda_{\text{max}} = 242$ nm, $\epsilon = 11400$) [14]. Since at the isosbestic points at 267 and 220 nm the extinction coefficients of TlCp and pentafulvene are roughly equal, the photolysis of TlCp generated fulvene in a 1:1 stoichiometry. The quantum yield for the formation of fulvene was dependent on the wavelength of irradiation ($\phi = 0.1$ at 254 nm and 0.008 at 313 nm). At later stages of the photolysis the isosbestic points were lost indicating secondary processes.

4. Discussion

The bonding in TlCp (and InCp) has been discussed extensively [15–19]. From these calculations a simple

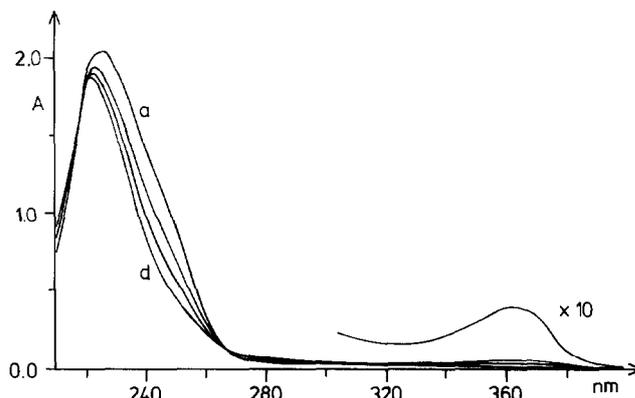


Fig. 2. Spectral changes during the photolysis of 2.58×10^{-4} M TlC_5H_5 in methanol at (a) 0 min and (d) 4 min irradiation time with $\lambda_{\text{irr}} = 254$ nm and a 1 cm cell.

MO scheme can be derived (Fig. 3). The most important MOs including the frontier orbitals are generated by the interaction of the s and p valence orbitals of the metal with the bonding π -orbitals of Cp^- . In this context it is interesting to note that the bonding in TlCp is quite similar to that in MCl_3^- with $\text{M} = \text{Ge}, \text{Sn}$ and Pb [5,20]. According to Fig. 3 the longest-wavelength absorption of TlCp at $\lambda_{\text{max}} = 280$ nm is assigned to the metal-centred $a_1 \rightarrow a_1^*, e_1^*$ sp transition from the lone pair at Tl^+ to the empty p-orbitals of the metal. It corresponds to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ sp transition of the free Tl^+ ion [3–5]. This assignment is supported by the appearance of the luminescence of TlCp since an emission is expected to show up only if sp transitions occur at lower energies than other transitions of different origin [3–5]. The more intense absorption of TlCp at $\lambda_{\text{max}} = 228$ nm is then assigned to the ligand-to-metal charge transfer (LMCT) transition $e_1 \rightarrow a_1^*, e_1^*$ (Fig.

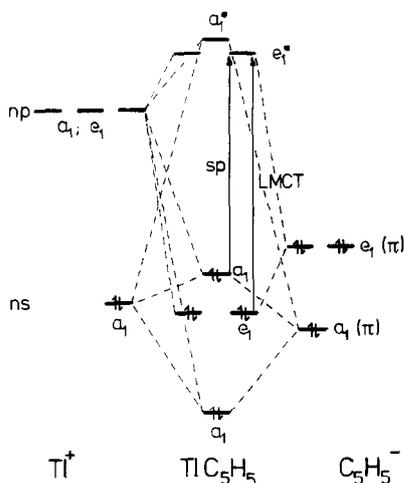


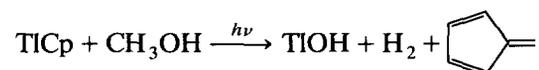
Fig. 3. Qualitative MO scheme of TlC_5H_5 (C_{5v} symmetry).

3) from the Cp^- ligand into the empty p-orbitals of thallium. It should be mentioned that the nature of the HOMO has been discussed amid some controversy. It was assumed to be either the a_1 lone pair [17,19] or the degenerate e_1 ligand orbital [15,18]. In the light of our results we prefer an a_1 assignment for the HOMO. However, both orbitals a_1 (lone pair) and e_1 (Cp^-) are certainly close in energy.

The emission of TlCp at $\lambda_{\text{max}} = 360$ nm is assumed to originate from the lowest sp excited state ($^3\text{P}_1$ of free Tl^+). The Stokes shift of this spin-forbidden transition is relatively small ($\Delta\bar{\nu}$ ca. 8000 cm^{-1}) indicating moderate structural changes in the excited state. This observation is not surprising since in distinction to other three-coordinate s^2 complexes such as MCl_3^- ($\text{M} = \text{Ge}, \text{Sn}$ and Pb) [5,20] TlCp cannot be transformed to a planar structure.

The photolysis of TlCp is assumed to be induced by $e_1 \rightarrow a_1^*$, e_1^* (Cp^- to Tl^+) LMCT excitation since the reaction is most efficient upon light absorption by the CT band. The appearance of the metal-centred luminescence and the lower photochemical quantum yield upon irradiation into the sp absorption at longer wavelength suggest that the reactive LMCT state can be also populated from the emitting sp state by an activated process. Similar arguments were used to explain the wavelength-dependent quantum yields for the reductive elimination of TeBr_6^{2-} [21].

The photolysis of TlCp in methanol can be described by the equation:



This reaction seems to be quite unique. At the moment we can offer only a tentative explanation. In the LMCT state TlCp roughly consists of a thallium atom and a Cp radical. This radical pair is certainly very reactive and could attack the solvent in the primary photochemical step. The primary products and the subsequent processes may be identified by further studies including flash photolysis and low-temperature spectroscopy.

As a final remark we would like to point out the potential of this photoreaction for a photocatalytic conversion of cyclopentadiene and methanol to pentafulvene. This idea is based on the fact that TlOH which is one of the photoproducts is well known to yield TlCp

thermally by its reaction with cyclopentadiene [13]. It may be necessary to carry out such a photocatalysis by a phase transfer photolysis [22] because fulvene seems itself to be light-sensitive. In order to prevent a secondary photolysis of fulvene it must be accumulated in a separate phase which is kept in the dark.

Acknowledgments

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