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Photochemistry of aqueous methyltrioxorhenium(VII). Intramolecular sensitization in the 2,2'-bipyridine adduct by ligand-to-ligand charge transfer excitation¹

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Abstract

Aqueous $\text{CH}_3\text{ReO}_3\text{bipy}$, which is formed by the addition of 2,2'-bipyridine (bipy) to a solution of CH_3ReO_3 , displays a long-wavelength ($\text{CH}_3^- \rightarrow \text{bipy}$) ligand-to-ligand charge transfer (LLCT) band at $\lambda_{\text{max}} = 360$ nm. Light absorption by this band leads to photolysis according to the equation $\text{CH}_3\text{ReO}_3\text{bipy} + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{bipyH}^+ + \text{ReO}_4^-$ ($\phi = 0.28$ at $\lambda_{\text{irr}} = 366$ nm). As shown in a previous study, the photolysis of the parent compound CH_3ReO_3 proceeds in a similar manner to the bipy adduct, but requires shorter wavelength irradiation corresponding to ($\text{CH}_3^- \rightarrow \text{Re}^{\text{VII}}$) ligand-to-metal charge transfer (LMCT) excitation.

Keywords: Rhenium complex; Charge transfer; Sensitization

1. Introduction

Organometallic oxides containing transition metals in high oxidation states have attracted much attention in recent years [1]. Despite this general interest, the photochemistry of these compounds is still largely unexplored although initial observations have revealed intriguing details [2,3]. Compounds of the type $\text{RRe}^{\text{VII}}\text{O}_3$, with $\text{R}^- \equiv \text{CH}_3^-$, C_2H_5^- and related carbanions, are characterized by reactive ligand-to-metal charge transfer (LMCT) states which induce photoredox processes in the primary photochemical step [2,3]. Owing to the d^0 electron configuration at Re^{VII} , excited states of different origin are not available to RReO_3 . However, since CH_3ReO_3 can easily expand its coordination sphere [4–9], the attachment of suitable ligands should provide ready access to other excited states. This approach may lead to a change in photochemistry. Recently, it has been demonstrated that, on addition of $[\text{Fe}(\text{CN})_6]^{4-}$, the binuclear complex $[\text{CH}_3\text{Re}^{\text{VII}}\text{O}_3\mu\text{-NCFe}^{\text{II}}(\text{CN})_5]^{4-}$ is formed, which undergoes photoredox decomposition on ($\text{Fe}^{\text{II}} \rightarrow \text{Re}^{\text{VII}}$) metal-to-metal charge transfer (MMCT) excitation [10]. In contrast with this observation, it is also feasible that the coordination of an appropriate new ligand may cause intramolec-

ular sensitization of the photochemistry of CH_3ReO_3 without changing the reaction pattern. We explored this possibility and selected the 2,2'-bipyridine (bipy) adduct of CH_3ReO_3 for the present study [5,7–9]. While CH_3ReO_3 is colourless, $\text{CH}_3\text{ReO}_3\text{bipy}$ is yellow. It is shown that the photoreactivity of CH_3ReO_3 [2,3] is preserved in the bipy adduct. However, in comparison with the parent compound, the photolysis of $\text{CH}_3\text{ReO}_3\text{bipy}$ can be sensitized by longer wavelength irradiation. This is possible because the absorption spectrum of the bipy adduct displays a new low-energy band which is assigned to a ($\text{CH}_3^- \rightarrow \text{bipy}$) ligand-to-ligand charge transfer (LLCT) transition. In this context, it is interesting that recent studies have demonstrated that LLCT excited states play a significant role in the spectroscopy and photochemistry of coordination compounds [11]. In the case of organometallic complexes, the importance of LLCT states, which involve the promotion of an electron from a carbanion ligand to an acceptor such as bipy or porphyrin, is just being recognized [12–18].

2. Experimental section

2.1. Materials

The compound methyltrioxorhenium was purchased from Aldrich (Nr. 41, 291-0) and used as received. Acetonitrile

¹ Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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was of spectrograde quality. The water used was triply distilled.

2.2. Photolyses

The light source was an Osram HBO 100 W/2 or Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using Schott PIL/IL interference filters (313, 333, 366 and 405 nm) or a Schoeffel GM 250/1 high-intensity monochromator (bandwidth, 23 nm). The photolyses were carried out in solutions of water and $\text{CH}_3\text{CN-H}_2\text{O}$ mixtures (9:1) in 1 cm spectrophotometer cells at room temperature. Solutions were air saturated since deaeration did not affect the results. The progress of photolysis was monitored by UV-visible spectrophotometry. The photoproducts were identified by their absorption spectra. For quantum yield determinations, complex concentrations giving essentially complete light absorption were used. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. The absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated and equipped with an RKP-345 detector.

2.3. Instrumentation

Absorption spectra were recorded on a Hewlett Packard 8452A diode array spectrometer or a Uvikon 860 double-beam spectrophotometer. The progress of photolysis was monitored by UV-visible spectral measurements. Gaseous products (CH_4 and C_2H_6) were identified by gas chromatography (Perkin Elmer 8500, headspace sampler HS-6).

3. Results

The electronic spectrum of $\text{CH}_3\text{ReO}_3\text{bipy}$ in CH_3CN displays absorption bands at $\lambda_{\text{max}} = 360$ nm ($\epsilon = 260$ l mol⁻¹ cm⁻¹), 306 nm ($\epsilon = 3700$ l mol⁻¹ cm⁻¹), 280 nm ($\epsilon = 16\,700$ l mol⁻¹ cm⁻¹) and 238 nm ($\epsilon = 16\,000$ l mol⁻¹ cm⁻¹). Solutions of $\text{CH}_3\text{ReO}_3\text{bipy}$ were also generated in

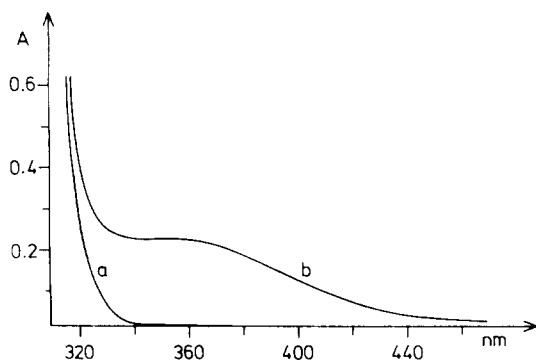


Fig. 1. Electronic absorption spectra of 2.0×10^{-3} M CH_3ReO_3 and 2.0×10^{-3} M bipyridine in water as separate solutions (a) and as a mixture (b) (1 cm tandem cell).

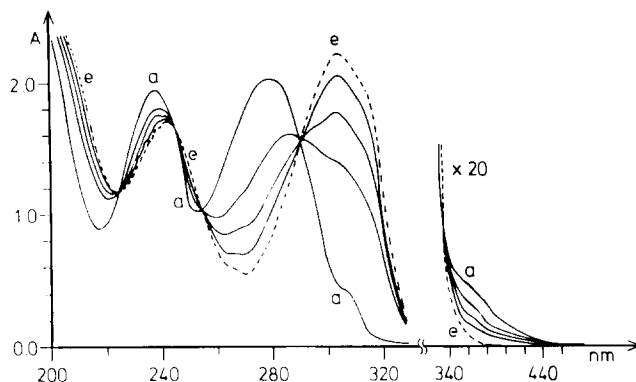


Fig. 2. Spectral changes during the photolysis of 1.22×10^{-4} M $\text{CH}_3\text{ReO}_3\text{bipy}$ in $\text{CH}_3\text{CN-H}_2\text{O}$ (9:1) at room temperature after 0 min (a) and 30 min (e) irradiation time with $\lambda_{\text{irr}} = 405$ nm; 1 cm cell.

situ by mixing equimolar amounts of bipy and CH_3ReO_3 in acetonitrile or water. A comparison of the spectra of the separate components (which are colourless) and their mixture (Fig. 1) reveals immediately the appearance of a new long-wavelength absorption at $\lambda_{\text{max}} = 360$ nm which causes the yellow colour of $\text{CH}_3\text{ReO}_3\text{bipy}$. This adduct is not very stable. It dissociates partially on dilution of the aqueous solution as indicated by the deviation of the 360 nm band from the Lambert-Beer law. The release of bipy is also accompanied by the appearance of the blue fluorescence ($\lambda_{\text{max}} = 325$ nm) of aqueous bipy.

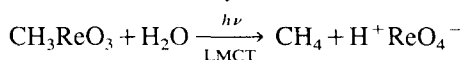
The photolysis of $\text{CH}_3\text{ReO}_3\text{bipy}$ is associated with spectral changes as shown in Fig. 2. Simultaneously, the pH of the solution decreases. At $\lambda_{\text{max}} = 305$ nm, a new band appears which is attributed to protonated bipy (bipyH^+ , $\lambda_{\text{max}} = 306$ nm, $\epsilon = 8200$ l mol⁻¹ cm⁻¹). As a further photoproduct, ReO_4^- is formed. The absorption spectrum of perrhenate displays a band at $\lambda_{\text{max}} = 235$ nm ($\epsilon = 3200$ l mol⁻¹ cm⁻¹) which is characterized by a vibrational structure [2]. This can also be recognized in the spectrum of the photolysed solution, although it is somewhat obscured by other photoproducts. This vibrational structure becomes more visible when the photolysis is carried out in acetonitrile containing 10% water (Fig. 2).

Finally, methane and traces of ethane are identified as additional photoproducts by gas chromatography. The photochemical loss of $\text{CH}_3\text{ReO}_3\text{bipy}$ was monitored by measuring the decrease in the optical density at $\lambda = 360$ nm. The disappearance quantum yield of $\text{CH}_3\text{ReO}_3\text{bipy}$ is $\phi = 0.28$ at $\lambda_{\text{irr}} = 366$ nm.

4. Discussion

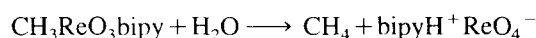
The electronic spectrum of CH_3ReO_3 is characterized by a long-wavelength absorption at $\lambda_{\text{max}} = 260$ nm, which has been assigned to an LMCT transition involving the promotion of an electron from the CH_3^- ligand to the d⁰ metal Re^{VII} [2]. LMCT excitation of aqueous CH_3ReO_3 induces a homolytic splitting of the Re-C σ bond in the primary photo-

chemical step. Secondary processes yield methane (and some ethane) and perrhenic acid as final products according to the overall stoichiometry [2,3]

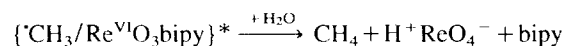
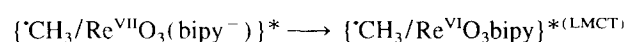


CH_3ReO_3 can easily expand its coordination sphere and accept an additional ligand [4–9]. A variety of such adducts $\text{CH}_3\text{ReO}_3\text{L}_n$ ($n = 1$ or 2), including $\text{CH}_3\text{ReO}_3\text{bipy}$ [5,7–9], have been prepared and characterized. While the $\text{CH}_3^- \rightarrow \text{Re}^{\text{VII}}$ LMCT transition of CH_3ReO_3 should be preserved in these adducts, additional electronic transitions depending on the nature of L may be introduced. In the case of $\text{L} \equiv \text{bipy}$, an LLCT transition from the methyl carbanion to bipy should occur in analogy with several other complexes which contain a metal–carbon σ bond and an acceptor ligand with low-energy π^* orbitals [12–18]. While CH_3ReO_3 is colourless, its bipy adduct is yellow. The long-wavelength band of $\text{CH}_3\text{ReO}_3\text{bipy}$ at $\lambda_{\text{max}} = 360$ nm which extends to the visible region is logically assigned to this LLCT transition. The absorptions at shorter wavelength are attributed to LMCT and bipy (π, π^*) inner ligand (IL) transitions. IL absorptions of bipy appear at wavelengths below 320 nm [19,20]. A detailed assignment of the shorter wavelength bands of $\text{CH}_3\text{ReO}_3\text{bipy}$ was not attempted since it is not relevant to this discussion.

The photolysis of $\text{CH}_3\text{ReO}_3\text{bipy}$ proceeds according to the overall stoichiometry



Product formation is assumed to take place in several consecutive steps



LLCT excitation involves the promotion of an electron from the Re–C σ bond into the π^* orbital of bipy. From the bipy ligand, this electron is transferred to Re^{VII} thus generating an LMCT excited state. This LMCT state finally yields stable products in close analogy with the photolysis of the parent complex CH_3ReO_3 [2,3]. The formation of small amounts of ethane takes place in a less efficient side reaction.

In terms of a potential energy diagram (Fig. 3), the LLCT excited state of $\text{CH}_3\text{ReO}_3\text{bipy}$ is deactivated to the reactive LMCT state. It is assumed that, in the LMCT state, the complex undergoes a larger distortion than in the LLCT state because the population of the Re–O π^* orbital (LMCT acceptor orbital) [2] affects the complex structure much more than the population of a ligand-localized π^* orbital. Accordingly, the optical LLCT transition requires less energy than direct LMCT excitation (Fig. 3). As a result, the pho-

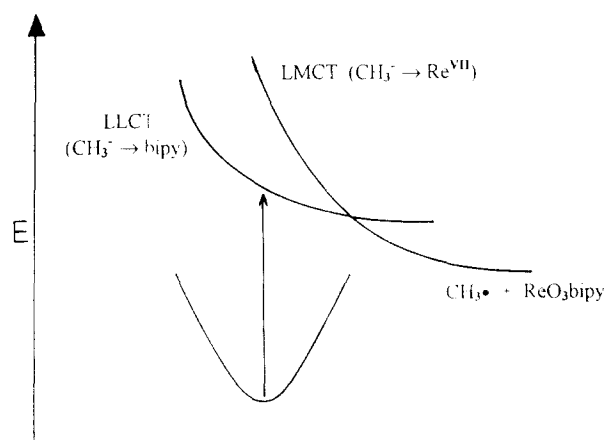


Fig. 3. Potential energy diagram of $\text{CH}_3\text{Re}^{\text{VII}}\text{O}_3\text{bipy}$.

tolysis of CH_3ReO_3 can be sensitized at longer wavelength via the formation of its bipy adduct and the concomitant introduction of a new low-energy excited state. In this context, it is interesting that the photolysis of methylcobalamin proceeds by a similar mechanism [18].

Acknowledgements

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