

Photochemistry of (*trans*-4-styrylpyridine) methyl(trioxo)rhenium(VII). Photoassisted isomerization of 4-styrylpyridine

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Abstract

The reflectance spectrum of solid $\text{MeReO}_3(\textit{trans}\text{-4-styrylpyridine})$ shows a long-wavelength band ($\lambda_{\text{max}} = 342 \text{ nm}$) with vibrational structure. This band is assigned to an intraligand transition of the coordinated styrylpyridine. In solution (e.g. CH_2Cl_2) the complex largely dissociates into MeReO_3 and styrylpyridine which displays a broad absorption at $\lambda_{\text{max}} = 308 \text{ nm}$. Irradiation with 366 nm light leads to selective excitation of residual amounts of intact $\text{MeReO}_3(\textit{trans}\text{-4-styrylpyridine})$ which undergoes a complete *trans*-to-*cis* photoisomerization of the coordinated ligand. Owing to the kinetic lability of $\text{MeReO}_3(\textit{trans}\text{-4-styrylpyridine})$ this photolysis proceeds as a photoassisted reaction of 4-styrylpyridine. © 1997 Elsevier Science S.A. All rights reserved.

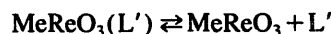
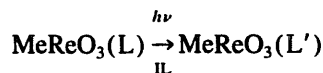
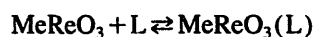
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1. Introduction

Organometallic oxides containing transition metals in high oxidation states have attracted much attention in recent years (for reviews on organometallic oxides in general, see Refs. [1]). The compound MeReO_3 is of particular interest since it forms the basis of an extensive chemistry including catalysis. A very important feature of MeReO_3 is its ability to expand its coordination sphere by the addition of further ligands [2,3]. By an appropriate choice of these ligands the excited state properties can be tuned. While the parent compound MeReO_3 is characterized by a photoreactive ligand-to-metal charge transfer excited state [4,5], reactive ligand-to-ligand charge transfer and metal-to-metal charge transfer states are introduced upon addition of bipy and $[\text{Fe}(\text{CN})_6]^{4-}$, respectively, as further ligands. The electronic spectra and photochemistry of the corresponding adducts $\text{MeReO}_3(\text{L})$ with $\text{L} = \text{bipy}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ have been studied quite recently [6,7]. As a further variation it is feasible to employ a ligand L with an excited state which keeps its reactivity upon coordination. We explored this possibility and selected *trans*-4-styrylpyridine (or *trans*-4-stilbazole) for the present study of a photoactive intraligand (IL) excited state. This choice was based on previous observations on the photochemistry of 4-styrylpyridine in the free and

coordinated state [8,9]. The comparison of the photoreactivity of $\text{XRe}^{\text{I}}(\text{CO})_3(\textit{trans}\text{-4-styrylpyridine})_2$ with $\text{X} = \text{Cl}, \text{Br}$ [9] and $\text{MeRe}^{\text{VII}}\text{O}_3(\textit{trans}\text{-4-styrylpyridine})$ should be rather intriguing because both complexes contain the same central metal, but in quite contrasting oxidation states.

The synthesis of $\text{MeReO}_3(\textit{trans}\text{-4-styrylpyridine})$ was anticipated not to be difficult. However, the study of compounds of the type $\text{MeReO}_3(\text{L})$ is generally hampered by their lability which results in an extensive dissociation in solution. While this is usually a serious drawback it offers a particular advantage for certain catalytic applications. In terms of photochemistry this system is well suited for a photoassisted reaction [10,11]:



The feasibility of a *trans/cis* isomerization of 4-styrylpyridine photoassisted by $\text{XRe}^{\text{I}}(\text{CO})_3(\textit{trans}\text{-4-styrylpyridine})_2$ has been considered before [9]. However, in contrast to the MeReO_3 adduct, the $\text{Re}(\text{I})$ complex is not a good candidate for this purpose since it is kinetically rather stable and does not easily exchange ligands.

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2. Experimental section

2.1. Materials

The compounds 4-styrylpyridine and MeReO_3 were purchased from Aldrich and used as received. The solvent dichloromethane was spectrograde.

2.2. Synthesis

2.2.1. $\text{MeReO}_3(\text{trans-4-styrylpyridine})$

To a solution of 0.50 g (0.002 mol) CH_3ReO_3 in 5 ml CH_2Cl_2 was added a solution of 0.362 g (0.002 mol) 4-styrylpyridine in 5 ml CH_2Cl_2 under stirring in the dark. The solution immediately turned yellow and crystals slowly precipitated. The analytically pure product was collected by filtration, washed with ether, and dried under vacuum; yield 0.68 g (79%). Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{NO}_3\text{Re}$: C, 39.06; H, 3.28; N, 3.25. Found: C, 38.97; H, 3.35; N, 3.22.

2.3. Photolyses

The light source was an Osram HBO 100 W/2. Monochromatic light was obtained by means of Schott PIL/IL interference filters 313 and 366 nm. The photolyses were carried out in solutions of CH_2Cl_2 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 and equipped with a RkP-345 detector.

2.4. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or a Shimadzu UV-2100 absorption spectrometer equipped with an integrating sphere accessory for reflectance spectra recording.

3. Results

The synthesis of $\text{MeReO}_3(\text{trans-4-styrylpyridine})$ is achieved simply by mixing solutions of MeReO_3 and *trans*-4-styrylpyridine in dichloromethane. The desired compound precipitates as yellow crystalline solid. The reflectance spectrum of this solid (Fig. 1) shows a long-wavelength band which is centered around 342 nm. This band displays a vibrational structure with features at $\lambda_{\text{max}} = 302, 326, 361$ and 372 nm.

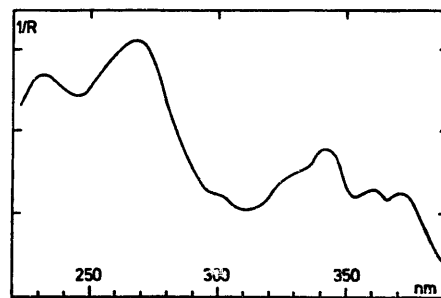


Fig. 1. Reflectance spectrum of $\text{MeReO}_3(\text{trans-4-styrylpyridine})$; $1/R$ (R = reflectance) in arbitrary units.

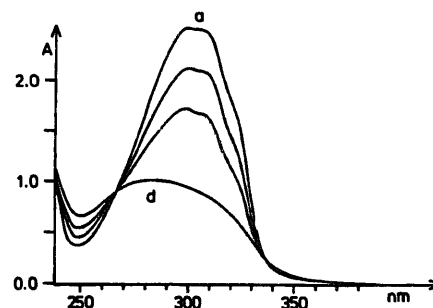


Fig. 2. Spectral changes during the photolysis of 8.38×10^{-5} M $\text{MeReO}_3(\text{trans-4-styrylpyridine})$ in CH_2Cl_2 at room temperature after 0 (a), 4, 8, and 16 (d) min irradiation time with $\lambda_{\text{irr}} = 366$ nm; 1 cm cell.

The solution spectrum (Fig. 2) shows an absorption at $\lambda_{\text{max}} = 308$ nm ($\epsilon = 29800$ l mol $^{-1}$ cm $^{-1}$). Upon irradiation of this solution with 313 nm light spectral variations are observed which include an isosbestic point at 266 nm. The final absorption spectrum contains a new maximum at $\lambda = 290$ nm. At very long irradiation periods the isosbestic point is lost indicating a secondary photolysis. When the irradiation was carried out with 366 nm light the spectral changes (Fig. 2) were essentially the same. However, photolysis can be driven further than that with 313 nm irradiation. The absorption maximum of the final spectrum is now shifted to $\lambda = 283$ nm (Fig. 2).

4. Discussion

Many complexes of the type $\text{MeReO}_3(\text{L})$ [3] including the compound with $\text{L} = \text{trans-4-styrylpyridine}$ can be easily prepared from their components MeReO_3 and L since they precipitate from solutions owing to their low solubility. However, these adducts are quite labile. At lower concentrations they are soluble but dissociate largely with the release of L . In the case of $\text{MeReO}_3(\text{trans-4-styrylpyridine})$ in CH_2Cl_2 this dissociation is indicated by the appearance of the absorption spectrum of free *trans*-4-styrylpyridine (Fig. 2) which shows a band maximum at $\lambda = 308$ nm ($\epsilon = 27900$) [9]. Accordingly, the electronic spectrum of the intact adduct $\text{MeReO}_3(\text{trans-4-styrylpyridine})$ can be only obtained for the solid compound (Fig. 1). The long-wavelength portion of this spectrum including the vibrational structure is very similar to the low-temperature absorption spectrum of

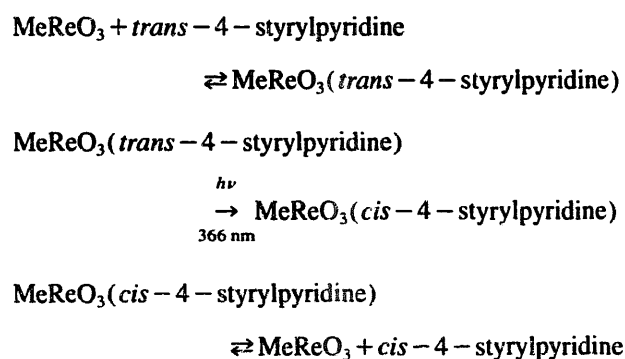
XRe(CO)₃(*trans*-4-styrylpyridine)₂ with X = Cl and Br [9]. In agreement with Wrighton's conclusion we assign the long-wavelength band of MeReO₃(*trans*-4-styrylpyridine) which is centered around 342 nm to an IL transition of the coordinated styrylpyridine.

As pointed out above the solution spectrum of MeReO₃(*trans*-4-styrylpyridine) shows the long-wavelength absorption of the free styrylpyridine at λ_{max} = 308 nm owing to an extensive dissociation of the adduct. However, this spectrum (Fig. 2) extends to about 385 nm while neither MeReO₃ [4] nor *trans*-4-styrylpyridine [9] absorb above 350 nm. This is a clear indication that the dissociation is not complete and the solution still contains a residual amount of the intact adduct which absorbs also above 350 nm (Fig. 1).

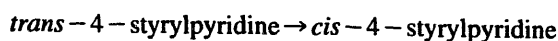
Upon 313 nm irradiation of solutions of MeReO₃(*trans*-4-styrylpyridine) in CH₂Cl₂ the light is absorbed almost exclusively by the free styrylpyridine. Accordingly, the results of the photolysis are very similar to those obtained for the free ligand which is well known to undergo an efficient *trans*-to-*cis* photoisomerization [8,9]. The 313 nm irradiation leads to a photostationary state with 88% of the *cis* isomer [9]. While the *cis* isomer absorbs at λ_{max} = 283 nm [12] the photostationary mixture shows a maximum at 290 nm.

When solutions of MeReO₃(*trans*-4-styrylpyridine) are photolyzed with 366 nm light only the intact adduct absorbs the radiation. In analogy to XRe(CO)₃(*trans*-4-styrylpyridine)₂ [9] the 366 nm irradiation of the intact adduct leads apparently to the population of a reactive IL excited state of the coordinated styrylpyridine which induces a facile *trans*-to-*cis* photoisomerization. A complete isomerization can be achieved as indicated by the final absorption spectrum of the photolyzed solution (Fig. 2) which shows the band maximum of the pure *cis*-4-styrylpyridine (λ_{max} = 283 nm; ε = 9450) [12].

Although this photochemical system is without any practical significance it represents an interesting case of a photoassisted reaction:



sum:



An important feature of this system is the kinetic lability of the adduct MeReO₃·*trans*-4-styrylpyridine in contrast to XRe(CO)₃(*trans*-4-styrylpyridine)₂ which is kinetically stable. It undergoes also a *trans*/*cis* photoisomerization of the coordinated ligand but does not readily release the styrylpyridine [9].

Acknowledgements

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