

Photochemistry of the 8-Quinolinol Adduct of Methyltrioxorhenium(VII)

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Abstract

MeReO₃ forms a violet adduct with oxine (8-quinolinol or 8-hydroxyquinoline). MeReO₃(oxine) shows a long-wavelength absorption at $\lambda_{\max} = 540$ nm which is assigned to a $\text{CH}_3^- \rightarrow \text{oxine}$ (ligand-ligand charge transfer) transition. LLCT excitation leads to the formation of methane and ReO₃(oxinate) as stable photoproducts with $\phi = 0.0015$ at $\lambda_{\text{irr}} = 546$ nm in CH₃CN. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Oxine (8-quinolinol or 8-hydroxyquinoline) forms complexes with most metals [1]. These compounds have been used for a variety of applications, in particular in analytical chemistry [2–6]. Many metal oxinates are well known to show an intraligand (IL) luminescence [7–24]. Aluminum oxinate is an important ingredient for LEDs [25,26]. The IL luminescence of metal oxinates can be quenched by electron transfer [18,27]. As excited state reductants they have been shown to act as sensitizers for semiconductors [28,29]. In this context it is quite surprising that there is only very little known on metal oxinates which are intrinsically photoreactive [30,31]. For a rational design of light-sensitive oxine complexes this ligand should be attached to a complex moiety which is known to be photoactive. We explored this approach and selected the organometallic compound CH₃Re^{VII}O₃ [32,33] for this purpose. Since this complex can expand its coordination sphere further ligands are easily attached. Moreover, the parent compound MeReO₃ and its derivatives of the type MeReO₃ × L are all light sensitive [34]. Accordingly, the desired complex of the composition MeReO₃(oxine) seems to be a promising candidate for the present study.

2. Experimental

2.1. Materials/instrumentation

All solvents were of spectrograde quality. MeReO₃ and 8-hydroxyquinoline were commercially available from Aldrich. Absorption spectra were measured on a Hewlett Packard 8452A diode array spectrometer. The light source used was an Osram HBO 200 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 23 nm). The photolyses were carried out in solutions of CH₃CN in 1 cm spectrophotometer cells at room temperature. 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 actinometry and equipped with a RkP-345 detector. Methane was identified by gas chromatography (Perkin Elmer 8500, headspace sampler HS-6).

2.2. Synthesis of CH₃ReO₃(oxine)

A solution of 1 g (4 mmol) CH₃ReO₃ in 10 ml acetone was added dropwise to a solution of 0.58 g (4 mmol) oxine in 9 ml acetone under stirring. Stirring was continued for 3 h in the dark. The precipitate of a dark-violet micro-crystalline

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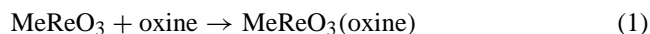
powder was collected by filtration, washed with small portions of acetone, then with ether, and finally dried under reduced pressure. Yield 1.1 g (70%). Analytically calculated for $C_{10}H_{10}NO_4Re$ (394.4): C = 30.45, H = 2.55, N = 3.55; found: C = 30.38, H = 2.51, N = 3.51.

2.3. Synthesis of $ReO_3(oxinate)$

A solution of 0.39 g (1 mmol) $MeReO_3(oxine)$ in 120 ml acetonitrile was photolyzed with a mercury middle-pressure lamp (Heraeus TQ 150 W) in a duran-glass ($\lambda_{irr} > 290$ nm) photoreactor under stirring. Stirring was continued until the evolution of methane finished (~ 40 min). The nearly colourless solution was concentrated by evaporation almost to dryness. The resulting orange crystals (yield: 0.19 g, 50%) were purified by recrystallisation from acetone/ether. Analytically calculated for $C_9H_6NO_4Re$ (378.35): C = 28.57, H = 1.60, N = 3.70; found: C = 28.51, H = 1.70, N = 3.63.

3. Results

The synthesis of our target compound was achieved by simply adding oxine to $MeReO_3$:



While the components oxine and $MeReO_3$ are colourless the resulting complex $MeReO_3(oxine)$ is dark violet. It is soluble in polar as well as less polar solvents such as CH_3CN or CH_2Cl_2 . The electronic spectrum of the compound in CH_3CN (Fig. 1) shows absorptions at $\lambda_{max} = 540$ ($\epsilon = 1800 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$), 352 (3300), 292 sh (5200) and 252 (31800) nm. $MeReO_3(oxine)$ is not luminescent but light sensitive. Solutions of $MeReO_3(oxine)$ are bleached by irradiation. As indicated by the spectral changes which are associated with the photolysis (Fig. 1) the photoproduct does not absorb above 450 nm. The disappearance of $MeReO_3(oxine)$ is monitored at $\lambda = 540$ nm. The complex

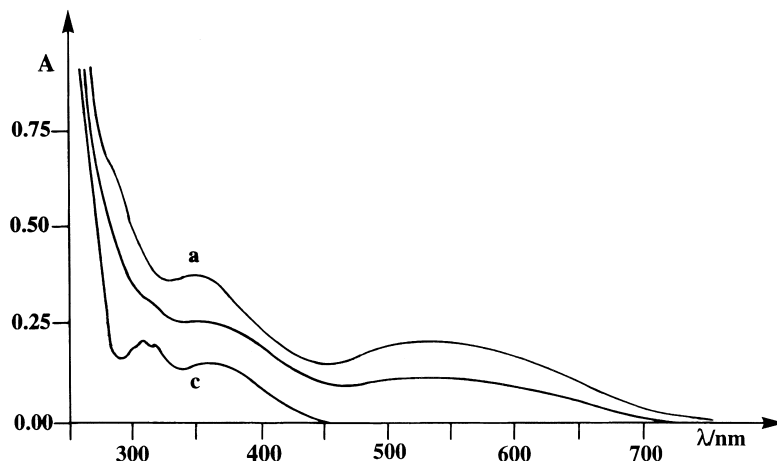
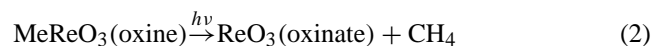


Fig. 1. Spectral changes during the photolysis of 1.22×10^{-4} M $MeReO_3(oxine)$ in CH_3CN at room temperature at 0 (a), 1 and (c) 5 min irradiation times with $\lambda_{irr} > 330$ nm (Osram HBO 200 W/2 lamp), 1 cm cell.

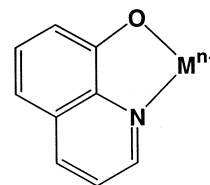
is photolyzed with $\phi = 0.0015$ at $\lambda_{irr} = 546$ nm. Since the photoproduct is not light-sensitive the photolysis can be driven to completion. The irradiation is accompanied by the evolution of methane which is identified by gas chromatography and collected in a gas-microburette. The volumetric determination of CH_4 ($MeReO_3(oxine)/CH_4 = 1.05 \pm 0.03$) is consistent with the following stoichiometry:



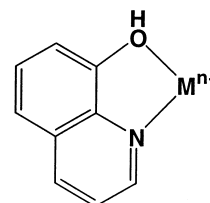
The photoproduct $ReO_3(oxinate)$ was isolated by the photolysis of $MeReO_3(oxine)$ in a preparative scale. The absorption spectrum of the analytically pure $ReO_3(oxinate)$ is identical to the final spectrum of Fig. 1.

4. Discussion

Generally, oxine coordinates in its deprotonated form (oxinate) as a bidentate ligand-metal cations [1]:



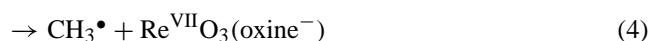
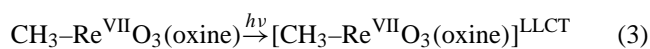
However, there are also many complexes known which contain oxine as a neutral ligand [1]:



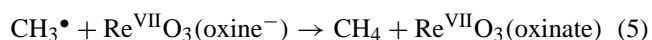
This latter coordination mode apparently applies to $MeReO_3(oxine)$.

The absorption spectra of oxinate complexes are frequently characterized by a longest-wavelength band around 400 nm which is assigned to an oxinate intraligand (IL) transition [8–24]. Oxinate does not seem to be a strong electron donor or acceptor since it does not participate in low-energy CT transitions. However, metal-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) absorptions of metal oxinates may occur at higher energies when reducing or oxidizing metals are present.

MeReO₃ displays a CH₃⁻ → Re^{VII} LMCT band at λ_{max} = 260 nm (in n-hexane) as lowest energy absorption [35,36]. The longest-wavelength absorption of MeReO₃(oxine) at λ_{max} = 540 nm which causes the striking violet colour of this compound is quite unexpected and not characteristic for MeReO₃ × L [34] or oxinate complexes [8–24]. We suggest that this band is assigned to a CH₃⁻ → oxine ligand-ligand charge transfer (LLCT) transition. This assignment is based on the following considerations. In addition to CH₃⁻ → Re^{VII} LMCT, low-energy CH₃⁻ → L CT transitions may occur in MeReO₃ × L complexes [37] provided L is a reasonable strong electron acceptor. This notion does not apply to the oxinate anion which is a weak acceptor. However, the protonation of the oxinate which generates the neutral oxine should increase the the acceptor strength considerably in analogy to the protonation of various other acceptor ligands [38]. Accordingly, a CH₃⁻ → oxine LLCT absorption is indeed expected to appear at rather long wavelength. The LLCT assignment of the 540 nm band is also supported by the photoreactivity of MeReO₃(oxine). LLCT excitation leads to the promotion of an electron from the CH₃-Re σ-bond into the π* orbitals of oxine. As a consequence a radical pair is formed:



The methyl radical which is also generated upon LMCT excitation of CH₃ReO₃ [34–36] is well known to efficiently abstract a hydrogen atom from any available substrate. In the case of the oxine radical anion hydrogen abstraction leads simply to the oxinate anion which finally coordinates to rhenium:



The photoproduct Re^{VII}O₃(oxinate) shows an absorption spectrum (Fig. 1) which is quite similar to that of many other oxinate complexes which are characterized by IL absorptions around 400 nm [8–24].

In summary, the complex MeReO₃(oxine) is a rare example of a light-sensitive oxine complex. In distinction to the oxinate anion, the neutral oxine is a relatively strong acceptor ligand. MeReO₃(oxine) is thus characterized by a long-wavelength CH₃⁻ → oxine LLCT absorption. LLCT excitation finally leads to the formation of methane and ReO₃(oxinate) as stable photoproducts.

Acknowledgements

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