

Investigations on the Redox-Photochromism of Rhodium Acetonitrile Complexes

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The spectroscopic and photochromic properties of the dinuclear rhodium complex $\text{Rh}_2\text{L}_{10}\text{X}_4$ ($\text{L} = \text{CH}_3\text{CN}$, $\text{X}^- = \text{BF}_4^-$) have been studied in acetonitrile solution. A reversible wavelength-dependent photoredox disproportionation of the dark-equilibrated dirhodium(II) compound occurs upon irradiation with quantum yields of $\phi = 0.04$ at 254 nm and $\phi = 0.60$ at 436 nm, respectively. While the photolysis products show conspicuous aggregation phenomena at higher concentrations, a straightforward pseudo-bimolecular recombination of the metastable fragments following second-order kinetics was observed in 5×10^{-5} M solution with $k = 0.18 \text{ l mol}^{-1} \text{ s}^{-1}$ at 295 K. Both spectroscopic and kinetic results are consistent with the heterolytic formation of mononuclear rhodium(I) and rhodium(III) acetonitrile complexes in the course of the photochemical reaction.

Key words: Photochemistry, Rhodium Complexes, Electronic Spectra, Redox Reactions, Photochromism

Introduction

Light-sensitive polynuclear transition metal complexes are attractive models for the elaboration of catalytic multielectron redox reactivity [1, 2]. Excited state reactions involving a dinuclear rhodium-rhodium moiety have recently been applied for a broad variety of processes such as photoinitiated cleavage of DNA [3], photochemical energy conversion [4] and the immobilization of catalytically active metal complexes in mesoporous materials [5]. In this context, an important feature of the dirhodium acetonitrile complex $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ is the possibility of a reversible photochemical cleavage of the metal-metal bond of the dinuclear rhodium core in solution [6, 7]. In the present study the wavelength dependence of this remarkable photochromic system and the corresponding quantum yields are reported. The formation of oligomeric species and the recombination kinetics of the photolysis fragments are discussed. According to the nature of the reactive excited state and the observed reaction products, a heterolytic cleavage of the metal-metal bond following photoinduced electron transfer is suggested as the predominant disproportionation pathway.

Experimental Section

The dinuclear rhodium compound $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ was prepared following the literature method [6, 8]. All experiments were carried out in argon-saturated acetonitrile of spectrograde quality. UV vis electronic spectra were recorded on a Kontron Uvikon 860 absorption spectrophotometer. Kinetic measurements were carried out at 295 K in a thermostated reaction cell. For the investigation of the luminescence properties, a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier was used. A Hanovia Xe/Hg 977 B-1 (1kW) lamp equipped with a Schoeffel GM 250-1 monochromator served as continuous wave irradiation source. Quantum yields were determined using a calibrated Polytec pyroelectric radiometer equipped with a RkP-345 detector.

Results and Discussion

The orange complex $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ contains a σ -single-bonded dirhodium core with pseudooctahedral geometry about each of the metal centers and a staggered orientation of the nitrile ligands [6]. In solution, the presence of the metal-metal bonded $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}]^{4+}$ cation is characterized by a sharp strong absorption band in the ultraviolet region and weak but chromophoric electronic transitions in the visible spectrum (Fig. 1).

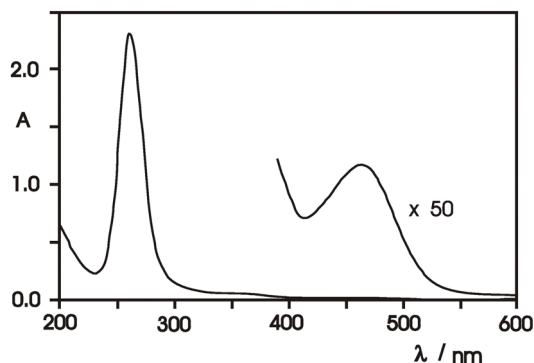


Fig. 1. Electronic absorption spectrum of $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}](\text{BF}_4)_4$ in acetonitrile solution, $c = 9.3 \times 10^{-4}$ M, 1-mm cell.

These spectral features with maxima at 261 nm ($24980 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 465 nm ($250 \text{ l mol}^{-1} \text{ cm}^{-1}$) are in good agreement with the reported literature values [7]. In the concentration range of 10^{-3} M to 10^{-5} M the solutions obey Lambert-Beer's law and no thermal decomposition occurs at 298 K. Since only acetonitrile ligands and BF_4^- counterions are present, the observed electronic transitions are expected to be of the metal-centered type (MC) and associated with the d-electrons of the dinuclear complex. The electronic structure of the two d^7 rhodium(II) centers can be described with a symmetrical $(d^6)d^1-d^1(d^6)$ configuration [1], which gives rise to lowest energy $d\sigma^*$ -excited states, whereas the $\sigma\sigma^*$ -excited states involving bonding electrons of the metal-metal core occur at higher energies.

In contrast to recent observations with excitation at 325 nm in the solid state [5], no authentic luminescence could be detected for the $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}]^{4+}$ cation in argon saturated acetonitrile solution at 298 K and in 77 K matrix. Irradiation of the samples resulted in a very efficient photochemical decomposition of the dinuclear complex, which was observed even under diffuse daylight. During photolysis of the compound new absorption bands were arising in the 300–450 nm spectral region, while the UV band of the dimer was rapidly bleached out (Fig. 2).

This photochemical reaction, suggesting a light-induced cleavage of the metal-metal bond, showed a pronounced wavelength dependence with quantum yields of dirhodium complex decomposition varying from $\phi = 0.04$ at 254 nm to $\phi = 0.60$ at 436 nm irradiation, respectively. The quantum yield profile clearly indicates that the reactive excited state respon-

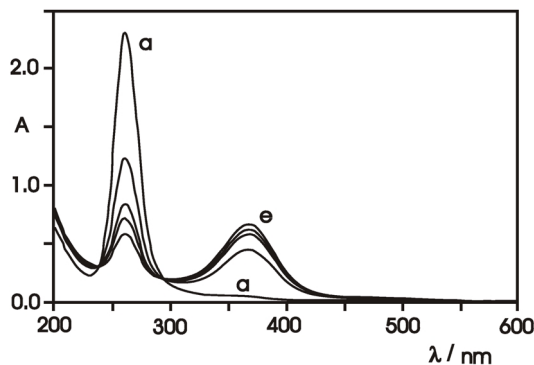
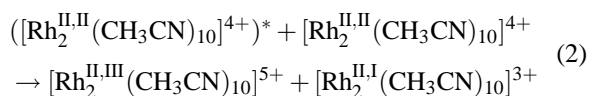
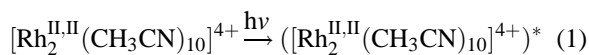


Fig. 2. Spectral variations during the photolysis of $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}](\text{BF}_4)_4$ in argon saturated acetonitrile at $t = 0$ (a), 10, 20, 30 and 50 s (e) irradiation times, $c = 9.3 \times 10^{-4}$ M, $\lambda_{\text{irr}} = 436$ nm, 1-mm cell.

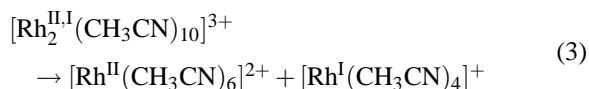
sible for the spectral changes observed under steady-state photolysis is more efficiently populated by irradiation in the region of the weak visible absorption bands of the $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}]^{4+}$ cation, corresponding to the low-lying $d\sigma^*$ electronic transitions of the complex (Fig. 1). On the other hand, the wavelength-dependence indicates that a homolytic cleavage of the Rh–Rh bond, which is the expected consequence of directly populating the energetically higher $\sigma\sigma^*$ -excited states of the dirhodium complex, does not lead to reaction products that can be observed in the time-window accessible in this study. A recent flash-photolysis investigation on the metal-metal bond photodissociation of rhodium acetonitrile complexes showed that odd-electron transient species do occur on timescales less than 100 ns [7]. Our present results, however, indicate that paramagnetic (d^7) homolysis products should rapidly recombine to the starting complex without significant contributions to the spectral changes obtained during continuous wave photolysis (Fig. 2). The surprisingly low photoproduct quantum yields upon UV irradiation are therefore attributed to a partial population of the reactive lower-lying $d\sigma^*$ -excited states competing with other $\sigma\sigma^*$ deactivation processes that may include homolysis followed by rapid radical recombination to the ground state $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}]^{4+}$ cation.

The efficient formation of photodissociation products upon long-wavelength irradiation can be explained without a homolytic primary step involved, when intermolecular processes are considered. It is well known, that the $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}]^{4+}$ cation easily undergoes irreversible reduction [6], and that the

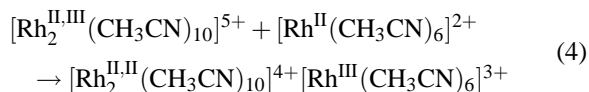
$d\sigma^*$ -excited states of dirhodium complexes display a rich multielectron photoredox reactivity [1]. In the absence of potential substrates that could react with the excited state compound, a photoinduced electron transfer process involving oxidative quenching by a second ground state dirhodium complex may therefore occur according to the following simplified reaction sequence (eqs (1–4)). The suggested heterolytic disproportionation pathway is initiated by a light-dependent charge separation step leading to mixed-valent dinuclear radical intermediates consistent with the results of flash-photolysis experiments (eq. (1) and (2)):



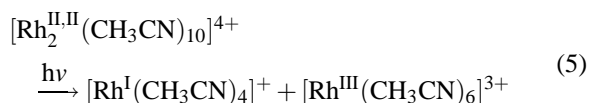
In the second step a fragmentation of the reduced odd-electron dimer occurs, which should be an unstable intermediate as suggested by electrochemical results [6] and thus compete with back electron transfer to the starting compounds (eq. (3)):



The disproportionation into diamagnetic two-electron-transfer products is suggested to be completed by a redox reaction between the remaining odd-electron species according to eq. (4):



Eq. (5) summarizes all these steps to an overall heterolytic metal-metal bond cleavage process as observed during steady state irradiation of the dinuclear rhodium complex:



In the concentration range typically applied for photochemical experiments (Fig. 2), the products of the light-induced disproportionation display conspicuous aggregation phenomena which seem to have complicated their identification and the elucidation of the reaction sequence in earlier studies. The formation of

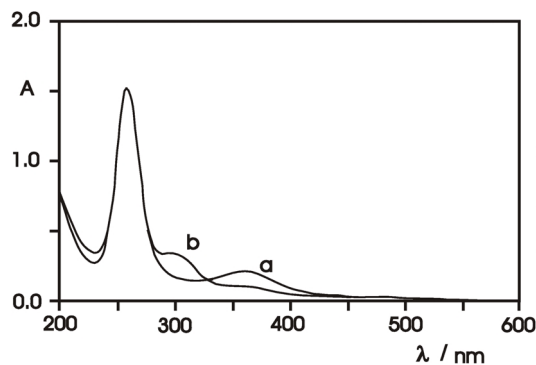


Fig. 3. Comparison of $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}](\text{BF}_4)_4$ photoproduct spectra at different overall complex concentrations. Deviations from Lambert-Beer's law are demonstrated for a partially photolyzed solution in acetonitrile at $c = 9.3 \times 10^{-4}$ M, 1-mm cell (a), and after dilution at $c = 9.3 \times 10^{-5}$ M, 1-cm cell (b).

oligomeric species after photolysis is clearly demonstrated by the experiment shown in Fig. 3.

Upon dilution of irradiated samples, the 366 nm absorption maximum of the apparent photoproduct is hypsochromically shifted to 303 nm and the spectral features around 230 nm disappear as well (Fig. 3). These data indicate that a dissociation of the species takes place as soon as lower concentrations are reached. Our results are similar to the concentration dependent spectral changes observed with rhodium(I) isocyanide complexes, which are known to form oligomeric species in acetonitrile solution [9]. The same behaviour is typical for many square planar d^8 metal complexes in solution. Therefore, taking into consideration the published data for related rhodium(I) acetonitrile complexes [7], the apparent photoproduct with an absorption maximum at 366 nm (Fig. 2) is ascribed to an aggregated form of the mononuclear $[\text{Rh}^{\text{I}}(\text{CH}_3\text{CN})_4]^+$ primary fragment of the photolysis (eq. (5)). The second metastable fragment $[\text{Rh}^{\text{III}}(\text{CH}_3\text{CN})_6]^{3+}$ which has to be postulated for the light-induced disproportionation according to eq. (5) is not unambiguously accessible to spectroscopic detection in our experiments. This is due to the fact that d^6 rhodium(III) complexes with neutral nitrogen ligands typically show two absorptions around 250 nm and 300 nm with extinction coefficients below $160 \text{ l mol}^{-1} \text{ cm}^{-1}$ [10]. In our case these absorptions are covered by stronger transitions in the same spectral region (Fig. 2). Nevertheless, the existence of the corresponding monomeric rhodium(III)

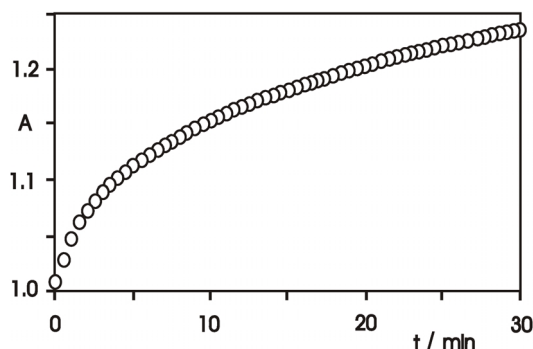


Fig. 4. Absorbance-time-profile during the thermal back reaction of a partially photolyzed sample (approx. 20% conversion at $t = 0$) in acetonitrile at 295 K, $c = 5 \times 10^{-5}$ M, 1-cm cell.

acetonitrile complex has recently also been demonstrated [11].

The absorption bands of photolyzed solutions are gradually changing when the samples are no longer irradiated. After a sufficiently long period in the dark, the initial spectral features of the dirhodium acetonitrile complex are completely regenerated. We have studied the kinetics of this recombination process by following the rising of the $\sigma\sigma^*$ -absorption band of

the $[\text{Rh}_2(\text{CH}_3\text{CN})_{10}]^{4+}$ cation at 261 nm with thermostated samples in the dark (Fig. 4).

In these experiments the rhodium concentrations were such as to avoid a significant presence of oligomeric species, while any contributions of the ligand concentration could be neglected in acetonitrile solution. It was found that the recombination process of the metastable photoproducts can be described with very good correlation as following a pseudo-second-order kinetics with $k = 0.18 \text{ l mol}^{-1} \text{ s}^{-1}$ at 295 K ($R = 0.9991$). With regard to the rhodium centers this process can be considered as the thermal reverse reaction of the overall photoinduced disproportionation shown in eq. (5). As a further support of this assumption it is important to note that very similar recombination reactions are well-known from previous investigations on the association of rhodium(I) and rhodium(III) isocyanide complexes in acetonitrile solution [12].

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