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Photochemical generation of nitroprusside induced by MLCT excitation of nitrosobenzenepentacyanoferrate(II)

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Abstract

Aqueous $[Fe^{II}(CN)_5(ONPh)]^{3-}$ shows a long-wavelength absorption at $\lambda_{max} = 528$ nm ($\varepsilon = 5300$) which is assigned to a MLCT transition terminating at the nitrosobenzene ligand. The photolysis initiated by MLCT excitation proceeds according to the equation $[Fe(CN)_5(ONPh)]^{3-} + H_2O \rightarrow [Fe(CN)_5NO]^{2-} + C_6H_6 + OH^-$. Nitroprusside is formed with $\phi = 0.03$ at $\lambda_{irr} = 546$ nm. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Nitric oxide (NO) plays a very important role in biological chemistry (for recent reviews see Refs. [1,2]). In this context metallonitrosyls have attracted much attention in recent years. It is well known that iron complexes participate in the generation and release of NO in biological systems. NO-synthase is an iron-containing enzyme which catalyzes the oxidation of arginine yielding finally NO (for recent reviews see Refs. [1,2]). Accordingly, the investigation of iron nitrosyl complexes is of considerable interest. In particular, the chemistry and biological effects of $[Fe(CN)_5NO]^{2-}$ (nitroprusside) have been studied in quite some detail [3]. While much work has been reported on the photochemistry of nitroprusside [3,4] its photochemical formation was not yet observed. We explored this possibility and selected $[Fe^{II}(CN)_5(ONPh)]^{3-}$ (Baudisch Complex) [5,6] as a promising candidate for the present study. The free ligand nitrosobenzene is light sensitive itself and photolyzes to NO and phenyl radicals [7–9].

2. Results

The electronic spectrum of aqueous $[Fe(CN)_5(ONPh)]^{3-}$ [10,11] (Fig. 1) shows absorptions at $\lambda_{max} = 528$ ($\varepsilon = 5300$ dm^3 M^{-1} cm^{-1}), 314 (4050) and 253 nm (7800). This solution is quite light sensitive. The photolysis of $[Fe(CN)_5(ONPh)]^{3-}$ is associated with spectral variations (Fig. 1) which include isosbestic points at $\lambda = 395$, 270 and 248 nm. These isosbestic points are preserved only at the beginning of the photolysis. The photoreaction is also accompanied by a pH increase and the formation of C_6H_6. Benzene was extracted from the aqueous solution with *n*-hexane and identified by its characteristic absorption spectrum which exhibits vibrational features at 280, 270, 262, 256, 250, 247 and 241 nm. These observations led to the supposition that $[Fe(CN)_5NO]^{2-}$ ($\lambda_{max} = 522$, 398, 330, 266 and 206 nm) might be a further photoproduct. A direct detection by an analysis of the spectral changes is, however, complicated by the interconversion of $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_5(NO_2)]^{4-}$ which is pH dependent [3,12]. Finally, an unambiguous confirmation for the formation of nitroprusside was achieved by its reaction with sulfide which generates the blue violet complex $[Fe^{II}(CN)_5(NOS)]^{4-}$ ($\lambda_{max} = 540$ nm, $\varepsilon = 6300$) [13]. Assuming a complete transformation of $[Fe(CN)_5(ONPh)]^{3-}$ to $[Fe(CN)_5NO]^{2-}$ the progress of the photolysis can be monitored by measuring the decrease of the optical density at 528 nm taking into account the extinction of the nitrosyl complex at this wavelength ($\varepsilon = 14$). However, only 80% of the nitrosyl complex calculated on the basis of this assumption is recovered as $[Fe(CN)_5(NOS)]^{4-}$ upon addition of sulfide. It follows that although the formation of the nitrosyl complex is the main reaction of the photolysis, side reactions take place, too. Neglecting this interference the quantum yield for the photoconversion of

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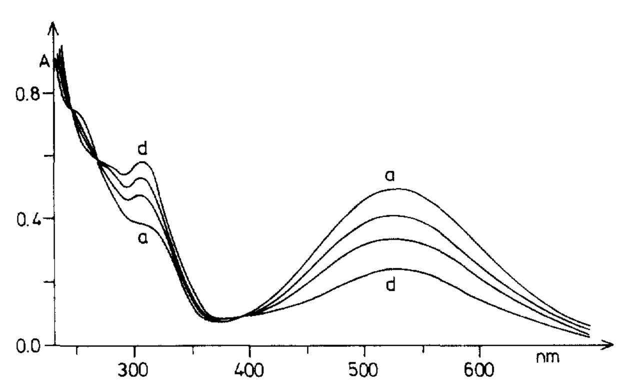

Fig. 1. Spectral changes during the photolysis of 9.38×10^{-5} M $[Fe(CN)_5(ONPh)]^{3-}$ in water at room temperature after 0 (a), 1, 2 and 4 (d) min irradiation time with $\lambda_{irr} = 546$ nm (1 kW Xe/Hg), 1 cm cell.

$[Fe(CN)_5(ONPh)]^{3-}$ to $[Fe(CN)_5NO]^{2-}$ is $\phi = 0.03$ at $\lambda_{irr} = 546$ nm.

3. Discussion

The electronic spectra of various $Fe^{II}(CN)_5L$ complexes have been studied for many years [14–16]. If L provides low-energy π^* orbitals intense MLCT absorptions appear in the visible spectral region and determine the colors of these compounds. Free nitrosobenzene displays two long-wavelength bands at $\lambda_{max} = 752$ ($\varepsilon = 43$) and 306 nm ($\varepsilon = 8000$) which belong to the lowest-energy $n\pi^*$ transitions [8]. The complex $[Fe(CN)_5(ONPh)]^{3-}$ shows a rather broad and intense absorption at $\lambda_{max} = 528$ nm (Fig. 1) which we assign to a MLCT transition in analogy to other complexes of the type $Fe^{II}(CN)_5L$. The shorter wavelength band of $[Fe(CN)_5(ONPh)]^{3-}$ at $\lambda_{max} = 314$ nm can be attributed to an intraligand transition of nitrosobenzene which undergoes a small bathochromic shift upon coordination. The weak $n\pi^*$ band of PhNO at $\lambda_{max} = 752$ nm was not identified in the spectrum of the complex but may be obscured by the intense MLCT absorption.

The majority of pentacyano complexes of iron(II) undergoes a photoaquation which is induced by LF excitation [4,17,18]:

$$[Fe^{II}(CN)_5L]^{3-} \xrightarrow{h\nu/H_2O} [Fe^{II}(CN)_5H_2O]^{3-} + L$$

If these complexes have available low-energy MLCT states photosubstitutions are less efficient since the population of reactive LF states competes with other deactivation modes [17]. However, in suitable cases MLCT states may be reactive, too [19]. Nitrosobenzene is light sensitive itself and decomposes to NO and phenyl radicals following $n\pi^*$ excitation [7–9]. Accordingly, it is not surprising that $[Fe(CN)_5(ONPh)]^{3-}$ is also photoactive, since

MLCT transitions terminate at π^* orbitals of coordinated nitrosobenzene. Indeed, $[Fe(CN)_5(ONPh)]^{3-}$ undergoes an efficient photolysis induced by MLCT excitation:

$$[Fe^{II}(CN)_5(ONPh)]^{3-} + H_2O \xrightarrow{h\nu} [Fe(CN)_5NO]^{2-} + C_6H_6 + OH^-$$

This observation can be rationalized by the following mechanism. In the MLCT state the nitrosobenzene ligand carries an additional negative charge which facilitates an electrophilic attack of a proton:

$$[Fe^{II}(CN)_5(ONPh)]^{3-} \xrightarrow{h\nu} \{[Fe^{III}(CN)_5(ONPh^-)]^{3-}\}^*$$

$$\{[Fe^{III}(CN)_5(ONPh^-)]^{3-}\}^* + H^+ \rightarrow [Fe^{III}(CN)_5(ONHPh)]^{2-}$$

The complex contains now the ligand ONHPh which is not a stable species but could decompose to benzene and NO. Finally, NO recombines with $[Fe^{III}(CN)_5]^{2-}$ to generate nitroprusside. Of course, the decomposition of ONHPh and the formation of nitroprusside may not be independent processes since the decay of ONHPh could occur in the coordination sphere of iron. A complete photoconversion of $[Fe(CN)_5(ONPh)]^{3-}$ to $[Fe(CN)_5NO]^{2-}$ is certainly not possible because nitroprusside is also photoactive in the same wavelength region [3,4] as the nitrosobenzene complex.

4. Conclusion

In summary, it should be emphasized that the complex $[Fe(CN)_5(ONPh)]^{3-}$ represents a novel example of reactive MLCT states. Moreover, the photochemical formation of $[Fe(CN)_5NO]^{2-}$ provides a new access to nitrosyl complexes. It is feasible that this type of photoreaction can be also applied to other metals.

Acknowledgements

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