

INTRAMOLECULAR EXCITED STATE ELECTRON TRANSFER FROM NAPHTHALENE TO COBALT(III)

A.H.Osman and A.Vogler

Institut für Anorganische Chemie der Universität Regensburg, Universitätsstr. 31,
8400 Regensburg, FRG

Introduction

The majority of intramolecular photoredox processes of metal complexes which have been reported ^{1,2)} takes place upon direct optical charge transfer (CT) excitation. As an alternative intramolecular photoredox processes may occur by an excited state electron transfer. An excited chromophoric group of a complex can undergo an electron transfer to or from another part of the same complex. While in intermolecular photoredox processes the structural arrangement of donor and acceptor in the encounter pair is not known intramolecular electron transfer occurs in a better defined environment. Although these features make it attractive to study intramolecular excited state electron transfer this subject has been largely neglected until a few years ago.

The recent interest in intramolecular excited state electron transfer is associated with attempts to understand the primary events of photosynthesis and to design model systems for the natural and an artificial photosynthesis. In the first step an excited state uphill electron transfer is required in order to convert light into chemical energy. In simple systems this first step is followed by a rapid downhill charge recombination. In the photosynthesis a charge separation is achieved by introducing a barrier for back electron transfer. Recently model compounds have been designed to study the charge separation in detail. A system which found much attention consists of a porphyrin as excited state electron donor which is linked covalently to a quinone as electron acceptor. In addition, a carotene may be attached as a donor to accomplish charge separation over large distances ³⁾.

T. J. Meyer and his research group have investigated the light-induced charge separation in compounds which contain metal complexes as initially excited chromophores ⁴⁾. In these cases the charge recombination regenerated the starting com-

pounds. Under suitable conditions another secondary reaction may be rapid enough to compete with the charge recombination. As a result stable photoproducts can be formed.

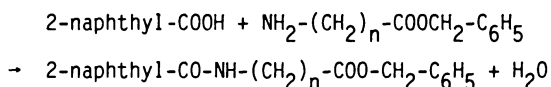
In 1969 Adamson et al. studied a photoreaction of this type ⁵⁾. Upon intra-ligand (IL) excitation of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{TSC}]^{2+}$ with $\text{TSC}^- = \text{trans-4-stilbene carboxylate}$ the excited TSC-ligand transfers an electron to $\text{Co}(\text{III})$ ⁶⁾. The $\text{Co}(\text{II})$ releases its ligands before an efficient charge recombination takes place. A variety of other complexes of the type $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{OOCR}]^{2+}$ with R = aromatic group such as naphthyl shows qualitatively the same behavior as the TSC complex ^{7,8)}. Excited state electron transfer from aromatic molecules to $\text{Co}(\text{III})$ amines takes place also as an intermolecular reaction ^{8,9)}. First observations were explained by the assumption that an energy transfer occurs to reactive CT states of the complex ⁹⁾. However, more recent investigations have shown that all results can be explained best by an excited state electron transfer mechanism ⁶⁻⁸⁾.

In the present study the complexes $[\text{2-naphthyl-CONH}-(\text{CH}_2)_n\text{-COOCo}^{\text{III}}(\text{NH}_3)_5]^{2+}$ with $n = 1$ to 5 were investigated in order to learn more about the structural requirements for excited state electron transfer in this system.

Results and Discussion

Synthesis

The free ligands were synthesized by the reaction of 2-naphthoic acid and the benzyl esters of the amino acids:



Saponification yielded the protonated ligands which were converted by NaOH to the sodium salts $\text{2-naphthyl-CO-NH}-(\text{CH}_2)_n\text{-COO}^-\text{Na}^+$. The complexes $[\text{2-naphthyl-CONH}-(\text{CH}_2)_n\text{-COOCo}(\text{NH}_3)_5]^{2+}$ were obtained as perchlorates by the reaction of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ and the sodium salts of the ligands. Recrystallization from acetone yielded analytically pure compounds.

Absorption Spectra

The electronic spectra of the sodium salts of the aqueous free ligands 2-naphthyl-CO-NH-(CH₂)_n-COO⁻Na⁺ show two absorption bands at $\lambda_{\max} = 310$ nm and $\lambda_{\max} = 317$ nm. Both bands which are of nearly the same intensity ($\epsilon \approx 1200$ L mol⁻¹ cm⁻¹) are assigned to $\pi\pi^*$ transitions of the naphthyl group. In the complex cations [2-naphthyl-CO-NH-(CH₂)_n-COOCo(NH₃)₅]²⁺ these intraligand (IL) bands appear with almost the same position and intensity. These results show unambiguously that the naphthalene moiety is an isolated chromophoric group of these complexes since coordination does not change the absorption spectrum of the free ligands. This observation is certainly not surprising because the aromatic π -electron system is separated by the saturated methylene groups ($n = 1$ to 5) from the Co³⁺ ion. In addition to the IL bands the first ligand field band of the complexes appears at $\lambda_{\max} = 504$ nm ($\epsilon = 85$).

Emission Spectra

Light absorption of the free ligands ($\lambda_{\text{exc}} = 310$ nm) is accompanied by an intense fluorescence ($\lambda_{\max} = 354$ nm) which originates from the lowest-energy $\pi\pi^*$ singlet of the naphthyl group. The lifetime was not measured but is known to be approximately 10^{-8} s for related naphthalene derivatives¹⁰). This emission is largely but not completely quenched in the complexes. The integrated fluorescence intensity was reduced to 2.00 % ($n = 1$), 1.75 % ($n = 2$), 1.48 % ($n = 3$), 1.07 % ($n = 4$), and 1.62 % ($n = 5$).

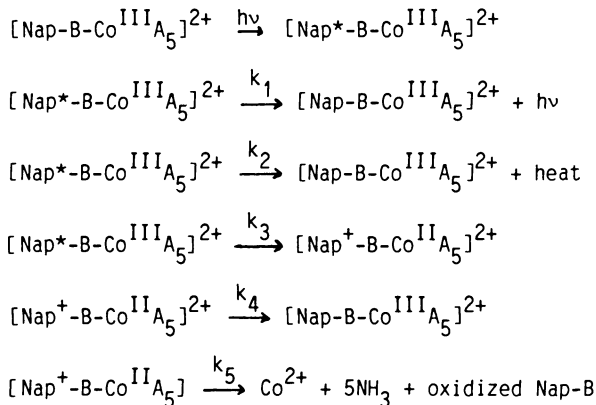
Photochemistry

Upon light absorption by the IL bands ($\lambda_{\text{exc}} = 333$ nm) the aqueous complexes underwent a photoredox reaction. While Co(III) was reduced to Co²⁺ the oxidation products were not identified. In analogy to related cases⁶⁻⁸) it is assumed that the naphthalene ligand was oxidized. The quantum yield of Co²⁺ formation was dependent on n : $\Phi = 0.084$ ($n = 1$), 0.072 ($n = 2$), 0.034 ($n = 3$), 0.024 ($n = 4$), and

0.041 ($n = 5$). In the concentration range of 10^{-2} to 10^{-3} M complex the quantum yields were constant. It follows that under these conditions the photoredox reaction is certainly an intra- and not an intermolecular process.

Mechanism

Naphthalene is oxidized at $E_{1/2} = 1.72$ V vs SCE ¹¹⁾. At an excitation energy of 3.97 eV ¹²⁾ the $\pi\pi^*$ singlet is now strongly reducing ($E_{1/2} = -2.25$ V). Although these parameters are certainly somewhat different from those of the ligands 2-naphthyl-CO-NH(CH₂)₂-COO⁻ there is no doubt that for the complexes there is a large driving force for an electron transfer from the excited 1L $\pi\pi^*$ singlet to the Co(III) center. Similar Co(III) complexes are reduced at $E^\circ = +0.06$ V ¹³⁾. Fluorescence quenching and formation of Co²⁺ can then be described by the following reaction scheme (Nap = 2-naphthyl group, B = -CO-NH-(CH₂)₂-COO- peptide bridge, A = ammonia):



On the basis of this reaction scheme kinetic equations can be derived:

$$\frac{\phi_o^F}{\phi_{\text{Co(III)}}^F} = 1 + \frac{k_3}{k_1 + k_2} = 1 + k_3 \cdot \tau_o$$

ϕ_o^F and $\phi_{\text{Co(III)}}^F$ are the fluorescence intensities of the free and coordinated ligands. τ_o is the lifetime of the $\pi\pi^*$ singlet of the free ligand which was assumed

to be 10^{-8} s (see above). The efficiency of electron transfer (ET) from the excited IL singlet to Co(III) is then given by:

$$\Phi_{\text{ET}} = \frac{k_3}{k_3 + \tau^{-1}}$$

The quantum yield of Co^{2+} formation is not only determined by Φ_{ET} but also by rate constants of back electron transfer (k_4) and of the decay of the Co(II) complex (k_5).

$$\Phi_{\text{Co}^{2+}} = \frac{\Phi_{\text{ET}} k_5}{k_5 + k_4}$$

The rate constant k_5 is not known but is assumed to be larger than 10^6 s^{-1} (14). It follows that the rate constants k_4 for back electron transfer can also not be obtained. However, relative rates k_4' were calculated assuming k_5 to be constant:

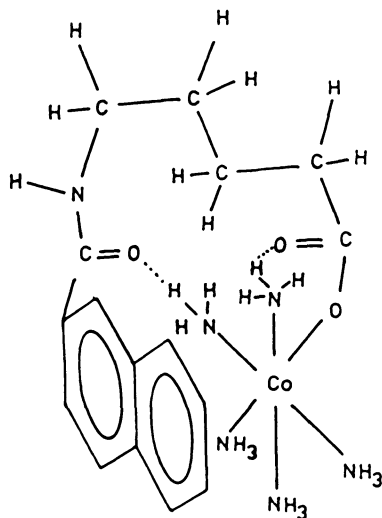
$$k_4' = \frac{k_4}{k_5} = \frac{\Phi_{\text{ET}}}{\Phi_{\text{Co}^{2+}}} - 1$$

Table 1.

Rate constants k_3 and quantum yields Φ_{ET} of excited state electron transfer, and relative rate constants k_4' of back electron transfer for [2-naphthyl-CO-NH-(CH_2)₂-COOC_o(NH₃)₅]²⁺.

n	$k_3 \times 10^{-9}$ s^{-1}	ET	k_4'
1	4.9	0.980	11
2	5.6	0.982	13
3	6.6	0.985	28
4	9.2	0.989	40
5	6.0	0.983	23

In contrast to the expectation it was found (Table 1) that the rate constant and efficiency of excited state electron transfer as well as the rate of back electron transfer drops from $n = 1$ to 4. This observation suggests that the actual distance between the naphthyl group and Co(III) decreases with increasing chain length of the peptide from $n = 1$ to 4. It is assumed that donor and acceptor come to a closer approach by an appropriate bending of the flexible peptide linkage. This back bonding may be favored by hydrogen bonding between coordinated ammonia and the carbonyl



groups of the peptide. At $n = 5$ electron transfer becomes less efficient (Table 1). The donor-acceptor distance may now increase by an extension of the peptide.

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