

Light Induced Electron Transfer of Metal Complexes

A. Vogler and H. Kunkely

Institut für Anorganische Chemie
Universität Regensburg
Universitätsstraße 31
D-8400 Regensburg (Germany)

Summary

Light induced electron transfer of metal complexes has been studied extensively during the last decade. This interest was stimulated by attempts to develop an artificial photosynthesis for the conversion and chemical storage of solar energy. Even if this goal has not yet been achieved photochemical redox processes of coordination compounds are now much better understood. In this review the various possibilities of photoinduced electron transfer are discussed and illustrated by selected examples. A distinction is made between intra- and intermolecular electron transfer which may occur as a direct optical transition or by an excited state electron transfer mechanism.

Introduction

The study of photochemical electron transfer processes involving coordination compounds (refs. 1-17) has become an important research subject during the last 10 years. These investigations were initiated, at least partially, by the desire to create an artificial photosynthetic system for the conversion and chemical storage of solar energy (refs. 18-20). It is well known that natural photosynthesis requires a light induced electron transfer as the basic process employing chlorophyll as the key compound. In order to imitate nature we have to improve our knowledge of photoredox processes. Coordination compounds, particularly those of transition metals, are excellent candidates for such studies. Metal complexes are generally redox active. Their lowest electronically excited states are frequently luminescent under ambient conditions. These properties facilitate the investigation of photochemical electron transfer reactions.

This review will illustrate the various possibilities of photoinduced electron transfer involving metal complexes. More recent developments and the interest of the authors are emphasized. A systematic approach requires a classification. As guide lines we applied two criteria. Intra- and intermolecular electron transfer are distinguished. In addition, electron transfer may occur by a direct optical transition or after an initial internal electronic excitation of the reductant or oxidant.

Finally, the extent of electronic coupling (refs. 8, 13 and 21-23) between the electron donor and acceptor is important. If the coupling is weak a "whole" electron changes its location. In the case of strong coupling which involves some electron delocalization between donor and acceptor only a fraction of an electron may be shifted.

In many cases the primary light induced electron transfer is followed by a rapid back electron transfer. Although a permanent photochemical change does then not occur such processes can be studied by time-resolved spectroscopy. However, under suitable conditions the charge separation is followed by efficient secondary reactions which compete successfully with the charge recombination. Consequently, stable photoproducts will be formed. In this review the latter situation is emphasized.

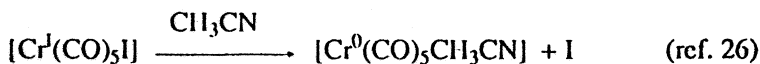
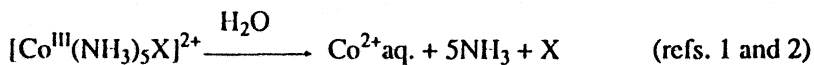
Intramolecular Electron Transfer

Direct Optical Charge Transfer

The majority of intramolecular photoredox processes of metal complexes which have been reported take place upon direct optical charge transfer (CT) excitation (refs. 1-11). Since metal complexes consist of metal centers and ligands they represent also the redox sites. The electronic interaction between these redox sites induces the occurrence of optical CT transitions which give rise to absorption bands in the electronic spectrum (ref. 24). Light absorption into these CT bands is associated with an electron transfer which may be followed by secondary reactions yielding stable photoproducts. Optical CT transitions are classified according to the redox sites (refs. 24 and 25): Ligand to Metal (LM), Metal to Ligand (ML), Metal to Metal (MM), Ligand to Ligand (LL), and Intraligand (IL). While LMCT and MLCT are the classical CT transitions MMCT, LLCT and ILCT are of more recent interest.

LMCT

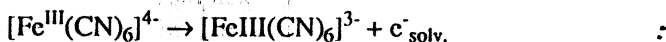
LMCT absorptions appear at low energies if the ligand is reducing and the metal oxidizing (ref. 24). Most Fe^{III} complexes are characterized by long-wavelength LMCT bands. Such absorptions cause also the colors of d^0 oxometallates such as CrO_4^{2-} and MnO_4^- . By definition a LMCT transition involves the reduction of the metal and oxidation of a ligand. In suitable cases the reduced metal is stabilized by secondary processes before a charge recombination regenerates the starting complex:



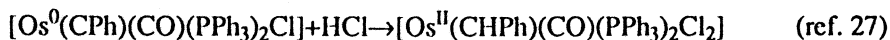
The oxidized ligand radicals X (halogen) undergo then further reactions.

MLCT

MLCT bands appear at long wavelength if the metal is reducing and a ligand provides empty orbitals at low energies (ref. 24). Complexes such as $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ and $\text{Ru}^{\text{II}}(\text{bipy})_3^{2+}$ (bipy = 2,2'-bipyridyl) are typical cases. Since the metal-ligand bonding does usually not change very much MLCT excitation induces rarely intramolecular photoreactions. For the same reason MLCT states are the most prominent luminescing excited states of coordination compounds. Nevertheless, MLCT excited complexes may undergo efficient intermolecular reactions such as excited state electron transfer (see below). A special type of excited state electron transfer is the generation of solvated electrons (refs. 1, 2 and 11):



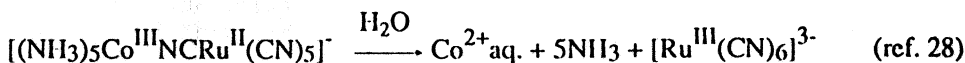
In the MLCT state a ligand-localized excess electron is transferred to the solvent. The solvent itself or another electron scavenger such as N_2O can be reduced irreversibly. As an alternative the electron-rich ligand of MLCT states is susceptible to an electrophilic attack. The addition of protons to coordinated carbynes illustrates this type of excited state reactivity:



MLCT excitation is associated with a shift of electron density from the metal to the carbyne ligand. In a limiting description the equilibrated excited state can be viewed as an Os^{II} complex which contains a deprotonated carbene ligand. A stabilization takes place by the addition of a proton to the coordinated carbene anion. The Os^{II} takes up a Cl^- ligand to complete its octahedral coordination.

MMCT

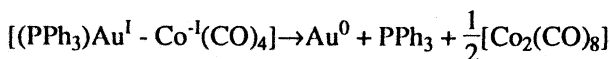
Since MMCT requires at least two metal centers it occurs only in bi- or poly-nuclear complexes which contain reducing and oxidizing metals (ref. 24). Both metals may be linked by a bridging ligand which mediates the electronic interaction. Typical examples are mixed-valence compounds which contain the same metal in two different oxidation states (refs. 13 and 21-23). The color of Prussian Blue which consists of $\text{Fe}^{\text{II}}-\text{CN}-\text{Fe}^{\text{III}}$ units is caused by a MMCT absorption involving an electronic transition from Fe^{II} to Fe^{III} . The MMCT excitation of suitable heteronuclear complexes induces a photoredox reaction (refs. 4,8):



Light absorption by the Ru^{II} to Co^{III} MMCT band creates the kinetically labile Co^{II} ammine complex. The decay of this complex competes successfully with back electron transfer. The metal-metal coupling in the $\text{Co}^{\text{III}}/\text{Ru}^{\text{II}}$ compound is rather weak.

The absorption spectrum of the binuclear complex is composed of the spectra of its mononuclear components and the additional MMCT band ($\lambda_{\text{max}}=375\text{nm}$).

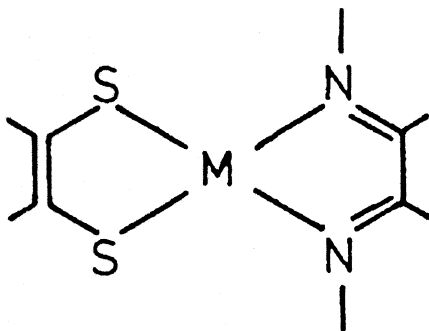
MMCT bands appear also in the spectra of polynuclear complexes which contain direct, but polar metal-metal bonds between metals of different electronegativity (refs. 29-31). Of course, the metal-metal coupling is strong in these cases and electron delocalization is only limited by the different energies of the overlapping metal orbitals. This type of polar metal-metal bond occurs in the complex $(\text{Ph}_3\text{P})\text{Au}^{\text{I}}-\text{Co}^{\text{I}}(\text{CO})_4$ (ref. 29). The absorption spectrum exhibits a low-energy Co^{I} to Au^{I} MMCT band. The MMCT transition involves the promotion of a $\sigma^{\text{b}}(\text{M}-\text{M})$ electron to a $\sigma^*(\text{M}-\text{M})$ orbital. Consequently, the MMCT ($\sigma^{\text{b}}\rightarrow\sigma^*$) excitation leads to a photoredox reaction which is associated with a homolytic cleavage of the polar metal-metal bond (ref. 29):



Metallic gold and cobalt carbonyl are the final products of the photolysis.

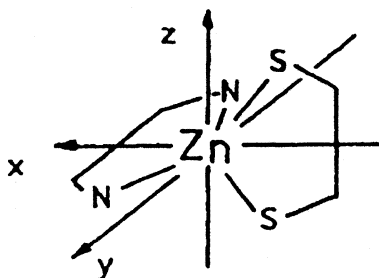
LLCT

Optical LLCT is only of recent interest (ref. 25). Such absorptions appear if one ligand is reducing and another oxidizing ($\text{L}_{\text{red}}-\text{M}-\text{L}_{\text{ox}}$). The metal only mediates and modifies the electronic ligand-ligand interaction. LLCT bands appear in the spectra of complexes such as $\text{Be}(\text{bipy})\text{X}_2$ with X^- =halide or alkyl anions. The color of these compounds is caused by X^- to bipy LLCT absorptions. LLCT bands are also exhibited by ligand-based mixed-valence complexes. An interesting family of such compounds contains 1,2-diimine (*e.g.* bipy) donor and 1,2-ethylenedithiolate acceptor ligands (ref. 25):



The basic electronic structure of both ligands is very similar but differs in their redox states by two electrons. The absorption spectrum of square planar d^8 complexes with $\text{M}^{\text{II}}=\text{Ni}^{\text{II}}$, Pd^{II} , and Pt^{II} is characterized by an intense dithiolate to diimine CT band which is strongly solvatochromic.

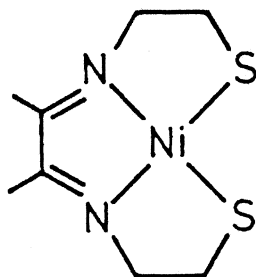
If M^{II} is Zn^{2+} the complexes are tetrahedral (ref. 32):



Due to the orthogonal orientation of the planes of both ligands the LLCT transition is symmetry-forbidden. The corresponding absorption is now of very low intensity. It has been suggested that these Zn^{II} complexes are good inorganic models for an efficient light-induced charge separation. The LLCT state has much in common with the so-called twisted intramolecular charge transfer (TICT) states of certain organic molecules (ref. 33).

ILCT

A ligand itself may consist of a reducing and oxidizing part (ref. 25). The spectrum of such a complex as well as that of the free ligand can then exhibit a ILCT band. Such an absorption was identified for the complex (ref. 34):



ILCT involves the transition from sulfur lone pairs to the diimine moiety.

Excited State Electron Transfer

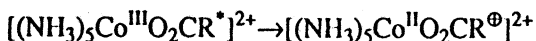
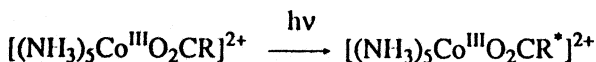
In distinction to the direct optical charge transfer an intramolecular photoredox process may also occur by an excited state electron transfer. An internally excited chromophoric group of a coordination compound can undergo an electron transfer to or from another part of the same molecule (ref. 8). This process is usually facilitated by large driving forces. Compared to ground states the reducing and oxidizing strength of excited states is increased by the amount of the excitation energy.

In many cases the excited state electron transfer is followed by a rapid back electron transfer which regenerates the starting complex. A net photolysis is thus not

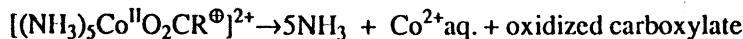
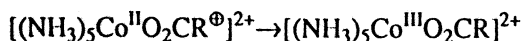
observed. Permanent photoproducts are only formed if the primary electron transfer yields labile species which undergo fast secondary reactions. Co^{III} ammine complexes are well suited as acceptors for irreversible electron transfer because Co^{II} ammines are not stable in aqueous solution but decay rapidly ($k \sim 10^6 \text{ s}^{-1}$) to $\text{Co}^{2+}\text{aq.}$ (ref. 35). Aromatic molecules may be used as excited state electron donors. They can be attached to Co^{III} ammines *via* a carboxylic group which coordinates to the metal (ref. 8).

A variety of complexes of the type $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{O}_2\text{CR}]^{2+}$ with e.g. R=1-,2-naphthalene, 4-stilbene, 9-anthracene, 4-biphenyl was studied (refs. 8 and 36). The interaction of donor and acceptor is certainly of the inner-sphere type. However, the electronic coupling is apparently weak. The donor and acceptor occur as independent chromophores of the complex. A LMCT band involving direct optical charge transfer from the aromatic group to Co^{III} does also not appear.

Light absorption by the aromatic substituent is associated with a complete fluorescence quenching indicating an efficient electron transfer from the excited $\pi\pi^*$ singlet state of R to Co^{III} (refs. 8 and 36) (* denotes an excited state):

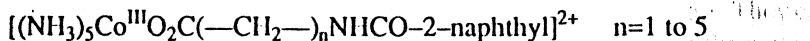


The electron transfer is certainly favored by a large driving force. The excited aromatic groups are very strong reductants ($E^0 < -2\text{V}$) while Co^{III} ammines are weakly oxidizing ($E^0 \sim +0.1\text{V}$). The product formation is determined by the competition between back electron transfer and decay of the Co^{II} ammine complex:



The quantum yield of Co^{2+} formation was very much dependent on R. A simple correlation was not apparent.

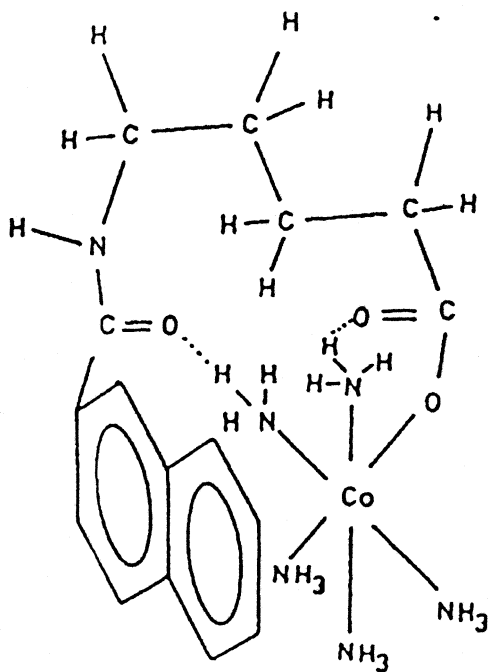
An interesting extension of this study included complexes of the type (ref. 37):



The excited state electron transfer within these complexes is still an intramolecular process but not by an inner-sphere mechanism since the methylene groups of the peptide linkage are electronically insulating. As a consequence the excited state electron transfer is not as efficient as that discussed above. This is indicated by the observation that the quenching of the naphthalene donor is not any more complete. Interestingly, the rate of excited state electron transfer increased from $k=4.9 \cdot 10^9 \text{ s}^{-1}$ for $n=1$ to $5.6 \cdot 10^9$ ($n=2$), $6.6 \cdot 10^9$ ($n=3$) and $9.2 \cdot 10^9$ ($n=4$) and dropped then to $6.0 \cdot 10^9 \text{ s}^{-1}$

for $n=5$ (ref. 38). The rate of back electron transfer is much slower: $k=1.07 \cdot 10^7 \text{ s}^{-1}$ ($n=1$), $1.26 \cdot 10^7$ ($n=2$), $2.71 \cdot 10^7$ ($n=3$), $4.02 \cdot 10^7$ ($n=4$), and $2.30 \cdot 10^7$ ($n=5$) (ref. 40). However, this transfer rate reaches also a maximum at $n=4$.

Generally, outer sphere electron transfer becomes slower with a larger distance between donor and acceptor. Our observation suggests that the actual distance between the naphthyl group and Co^{III} decreases with an 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 bridge if n grows from 1 to 4. This approach may be favored by hydrogen bonding between coordinated ammonia of the $\text{Co}(\text{NH}_3)_5$ moiety and the carbonyl group of the peptide linkage (ref. 37):



At $n=5$ electron transfer slows down in both directions. The donor-acceptor distance may now increase by an extension of the peptide chain.

Intermolecular Electron Transfer

While the intramolecular coupling between an electron donor and acceptor may vary considerably (ref. 8) the intermolecular interaction is generally much weaker. Nevertheless, light induced outer sphere electron transfer may take place by a direct optical CT transition or by a bimolecular encounter of an excited donor (or acceptor) with a ground state acceptor (or donor).

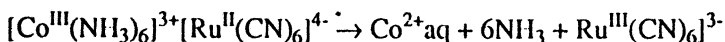
Direct Optical Charge Transfer

An optical intermolecular or outer sphere (OS) CT transition can occur if a reducing and an oxidizing molecule or ion are in close contact which provides some orbital overlap between donor and acceptor. This close contact is frequently facilitated by the electrostatic attraction within an ion pair (refs. 4-7, 9-11 and 17). But also neutral molecules may be close enough in suitable cases, particularly at high concentrations in solution or in the solid state (ref. 17).

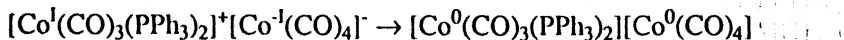
In analogy to intramolecular CT transitions (see above) optical OS CT can be classified according to the predominant localization of the donor and acceptor orbitals at the metal or ligand. Under appropriate conditions OS MLCT, LMCT, MMCT, and LLCT absorption bands will be observed (ref. 17).

The ion pair $[\text{Rh}^{\text{III}}(\text{bipy})_3]^{3+} [\text{Ru}^{\text{II}}(\text{CN})_6]^{4-}$ provides an example of OS MLCT (ref. 41). The electronic spectrum of the aqueous ion pair displays a new absorption which is assigned to a CT transition from Ru^{II} of the cyano complex anion to the bipy ligands of the rhodium complex cation. This OS MLCT band appears at much shorter wavelength ($\lambda_{\text{max}} = 379 \text{ nm}$) compared to the corresponding inner sphere MLCT absorption of $\text{Ru}^{\text{II}}(\text{bipy})_3^{2+}$ ($\lambda_{\text{max}} = 448 \text{ nm}$) (ref. 24). This shift seems to reflect the larger distance between Ru^{II} and bipy in the ion pair.

The aqueous ion pair $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+} [\text{Ru}^{\text{II}}(\text{CN})_6]^{4-}$ shows a Ru^{II} to Co^{III} MMCT band at $\lambda_{\text{max}} = 344 \text{ nm}$ (refs. 17 and 42). It is quite interesting that this absorption appears at $\lambda_{\text{max}} = 375 \text{ nm}$ for the binuclear complex $[(\text{NH}_3)_5\text{Co}^{\text{III}}\text{NCRu}^{\text{II}}(\text{CN})_5]^-$ (ref. 28). Again, the decreasing distance between the redox sites decreases also the energy of the CT transition. Of course, this conclusion is based on the assumption the electronic coupling is weak in both cases. Upon MMCT excitation the ion pair undergoes a photoredox decomposition quite analogous to that of the binuclear complex (see above) (refs. 17, 42 and 43):



A large number of organometallic salts consist of an oxidizing metal carbonyl or metallocenium cation and a reducing metal carbonyl anion (ref. 17). It has been shown quite recently that the intense colors of these salts originate from OS MMCT absorptions (refs. 17 and 44). For example, the ion pair $[\text{Co}^{\text{I}}(\text{CO})_3(\text{PPh}_3)_2]^+ [\text{Co}^{\text{I}}(\text{CO})_4]^-$ displays an Co^{I} to Co^{I} MMCT band at $\lambda_{\text{max}} = 386 \text{ nm}$ in acetone (ref. 45). The MMCT excitation creates a radical pair in the first step. These radicals are labile and undergo ligand dissociation and exchange reactions before they finally to form a metal-metal bond (ref. 45):

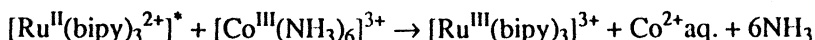


It is now recognized that light-induced electron transfer plays an important role in organometallic chemistry (refs. 17 and 44).

Excited State Electron Transfer

As pointed out above any electronically excited molecule is a much stronger reductant and oxidant than the same molecule in its ground state. Accordingly, intermolecular excited state electron transfer may take place while it does not occur in the ground state owing to thermodynamic limitations. However, the diffusional encounter must take place before the excited molecule is deactivated to the ground state. Generally, only the lowest excited states are long-lived enough to undergo a bimolecular electron exchange. If the molecule is luminescent the emission quenching by an acceptor or donor can be used to obtain kinetic data on the excited state electron transfer.

The first example of a transition metal complex which participates in excited state electron transfer was reported by Gafney and Adamson in 1972 (ref. 46):

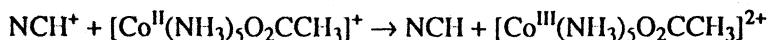
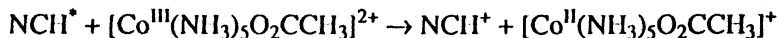


Since then numerous studies of intermolecular excited state electron transfer were carried out. The majority of investigations involved $\text{Ru}(\text{bipy})_3^{2+}$ and related complexes as excited donors or acceptors (refs. 9, 10, 12, 47 and 48). The ruthenium complex (refs. 47 and 48) offers many advantages for such studies. It can be reversibly reduced and oxidized. The lowest excited state which is a MLCT triplet undergoes an efficient and relatively slow ($\tau \sim 1 \mu\text{s}$) phosphorescence under ambient conditions. The excited state redox potentials for the couples $\text{Ru}(\text{bipy})_3^{2+*/3+}$ and $\text{Ru}(\text{bipy})_3^{3+/2+*}$ are $E^0 = -0.86 \text{ V}$ and $E^0 = +0.84 \text{ V}$. In aqueous solution the complex is thermally and photochemically quite stable.

However, all attempts to utilize $\text{Ru}(\text{bipy})_3^{2+}$ as sensitizer for the conversion and chemical storage of solar energy did not lead to any practical applications. The light induced charge separation yields primary redox products with a large potential difference which favors a rapid electron transfer. The absorbed light is then simply converted to heat. All attempts to slow down the charge recombination and to couple the primary electron transfer step to secondary reactions yielding kinetically stable products with a high energy content were not yet successful. Most efforts were directed toward the photochemical splitting of water. While first results were rather promising the final goal has not yet been achieved. Nevertheless, as a spin-off these investigations were beneficial for a better understanding of electron transfer reactions. The theories developed by Marcus, Hush, and others could be tested and extended (ref. 49).

At this point we will briefly discuss an example of intermolecular excited state electron transfer to illustrate the mechanism. In this case a comparison with a corresponding intramolecular electron transfer is quite interesting and informative. Naph-

thalene carboxylate cannot only be used as sensitizer for intramolecular (see above) but also for intermolecular excited state electron transfer to Co^{III} ammine complexes such as $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{O}_2\text{CCH}_3^{2+}$. The sequence of events may be described by the following simplified scheme (NC^- = 1-naphthalenecarboxylate) (ref. 50):



Electron transfer from the excited $\pi\pi^*$ singlet of NCH to the Co^{III} complex is associated with the fluorescence quenching of NCH and the irreversible formation of Co^{2+} . The analysis of the Stern-Volmer plot (Fig. 1) shows that the excited state electron transfer is very fast ($k=3.6 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (ref. 38) and takes place with an efficiency of almost unity.

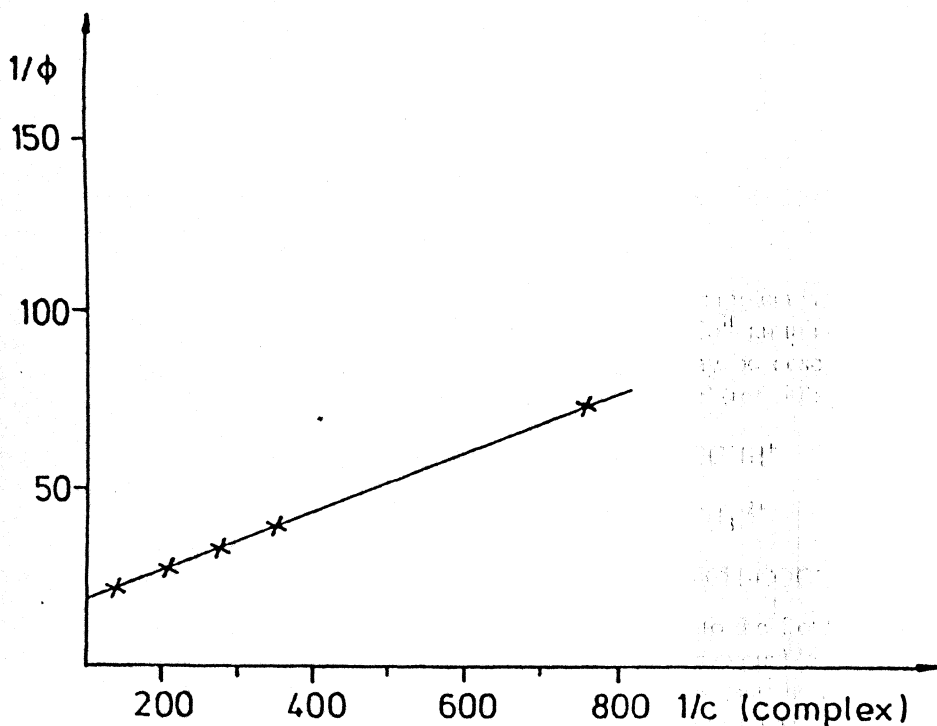


Fig. 1. Excited state electron transfer from 1-naphthalenecarboxylic acid ($8 \cdot 10^{-4} \text{ M}$) to $\text{Co}(\text{NH}_3)_5$ acetate $^{2+}$ (c in M) in a mixture of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1) and HClO_4 (0.01 M); Stern-Volmer plot of the reciprocal quantum yield (ϕ) of Co^{2+} formation vs. the reciprocal concentration of $\text{Co}(\text{NH}_3)_5$ acetate $^{2+}$.

This is a consequence of the large driving force. In its first excited singlet state naphthalene is strongly reducing ($E_{1/2} = -2.25$ V vs. SCE) while Co^{III} ammine complexes are weak oxidants ($E^0 \sim 0.1$ V) (ref. 37). On the contrary, the back electron transfer is much slower ($k = 4 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (ref. 40) and reduces the limiting quantum yield for Co^{2+} production to $\phi = 0.2$.

The intramolecular excited state electron transfer in $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{NC}]^{2+}$ must be also rather fast and efficient since the fluorescence of the coordinated NC^- is completely quenched. However, the quantum yield of Co^{2+} formation ($\phi = 0.005$) is now much lower. If all other processes occur with the same rates for inter- and intramolecular electron transfer the charge recombination in $\text{Co}(\text{NH}_3)_5\text{NC}^{2+}$ is much faster ($k = 2 \cdot 10^8 \text{ s}^{-1}$) than that for the bimolecular reaction (see above). At moderate driving forces the electron transfer is apparently facilitated by an inner-sphere mechanism.

The systems which were studied for applications in solar energy conversion suffer by an efficient energy-wasting charge recombination. In order to slow down this process various approaches were suggested (ref. 51). In natural systems electron transfer across an interface which may be a cell membrane seems to be important. In an attempt to imitate nature many studies were devoted to heterogeneous excited state electron transfer (ref. 51). Microheterogeneous environments were created by the application of micelles, vesicles, microemulsions and similar systems. A very simple model for a membrane is formed by the interface between two immiscible solvents. If the electron donor is soluble only in one phase and the acceptor in the other solvent an excited state electron transfer may take place across the interface. We explored this possibility and dissolved naphthalene in hexadecane and $\text{Co}(\text{NH}_3)_6^{3+}$ in water (0.1 M HCl) (ref. 52). In a simple pyrex beaker both solutions formed two immiscible layers. A vertical light beam passed the layer and was absorbed by the naphthalene in the top layer near the interface. As a result $\text{Co}(\text{NH}_3)_6^{3+}$ was reduced in the aqueous layer. The excited naphthalene apparently transferred an electron to $\text{Co}(\text{NH}_3)_6^{3+}$ across the interface of both immiscible solvents. A decrease of concentration of $\text{Co}(\text{NH}_3)_6^{3+}$ led also to a drop of the quantum yield of Co^{2+} formation. A nearly linear Stern-Volmer relationship was obtained when $1/[\text{Co}(\text{NH}_3)_6^{3+}]$ was plotted *versus* $1/\phi_{\text{rel.}}(\text{Co}^{2+})$. However, naphthalene is soluble in water to a small extent. Accordingly, Co^{2+} was not only generated by heterogeneous electron transfer across the interface but also by homogeneous electron transfer in the aqueous phase. Since we were not able to separate both processes the mechanistic implications of these observations are not yet clear.

Acknowledgment

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