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Coordination Chemistry Reviews 229 (2002) 147–152
COORDINATION CHEMISTRY REVIEWS
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Outer-sphere charge transfer in ion pairs with hydridic, carbanionic, sulfidic and peroxidic anions as electron donors—spectroscopy and photochemistry

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Received 6 June 2001; accepted 14 December 2001

Contents

Abstract

Ionic transition metal complexes are well known to participate in optical outer-sphere charge transfer (OSCT) of ion pairs which consist of oxidizing cations and reducing anions. Frequently, simple anions such as iodide or oxalate have been used as electron donors. Unfortunately, many important anions such as H^-, $C_6H_5^-$, S^{2-} and O_2^{2-} are not suitable owing to their strong nucleophilicity. However, this nucleophilicity can be attenuated if these anions are replaced by appropriate derivatives including BH_3CN^- as hydridic, $B(C_6H_5)_4^-$ as carbanionic, PO_3S^{3-} as sulfidic and BO_3^- as peroxidic donors. A variety of ion pairs which contain such anions and cationic transition metal complexes or organic cations are characterized by OSCT absorptions in their electronic spectra. Many ion pairs of this type are photoactive upon OSCT excitation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Charge transfer; Ion pairs; Electronic spectra; Photochemistry

1. Introduction

Charge transfer (CT) transitions play an important role in electronic spectroscopy [1,2] and photochemistry [3,4] of coordination compounds. Such CT transitions may be of the ligand-to-metal charge transfer (LMCT), metal-to-ligand charge transfer (MLCT), metal-to-metal charge transfer (MMCT), ligand-to-ligand charge transfer (LLCT) or intraligand charge transfer (ILCT) type [2,4]. In addition to these intramolecular (or inner-sphere, IS) CT transitions, outer-sphere charge transfer (OSCT) transitions may occur [5–7]. These OSCT interactions take place between non-bonded molecules or ions. Frequently, OSCT excitation leads to photochemical reactions [5–7].

Although OSCT interactions also exist between neutral molecules they are facilitated in ion pairs by electrostatic attraction [5–7]. There is an obvious analogy between ISCT and OSCT. For example, iodide serves as a donor for Co(III) in both cases.

$[Co^{III}(NH_3)_5I]^{2+}$ *ISCT*

$[Co^{III}(NH_3)_6]^{3+}I^-$ *OSCT*

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PII: S0010-8545(01)00473-8

For $[Co(NH_3)_5I]^{2+}$ the ISCT transition is of the LMCT type. In the following discussion the attention is drawn mainly to four donor anions which play a prominent role as reductants in general and as donor ligands in particular:

hydride carbanions sulfide peroxide.

When these ligands are coordinated to oxidizing metals low-energy LMCT transitions should occur. This is well known for complexes with carbanions, sulfide and peroxide as ligands, but insufficiently documented for hydride complexes [2]. Unfortunately, H^-, R^-, S^{2-} and O_2^{2-} apparently cannot be used as OSCT donors in ion pairs owing to the strong nucleophilicity of these anions which will react with a variety of electrophiles, in particular with protic solvents. However, if these anions are attached to suitable molecules or ions this nucleophilicity can be avoided while their reducing properties are preserved largely. Our observations on OSCT transitions involving such hydridic, carbanions, sulfidic and peroxidic donor anions are summarized in this report. Some relevant aspects of hydridic and carbanionic electron donors have been reviewed by Kaim quite recently [8].

2. Hydridic donor anions

The most versatile hydridic reductants are the boranates, in particular BH_4^- as the parent of all hydridoborates. Unfortunately, attempts to use BH_4^- as CT donor in ion pairs have not yet been successful due to its reactivity. For example, BH_4^- undergoes a facile hydrolysis in the presence of water and reduces even weak oxidants. The most stable boranate is $B_{12}H_{12}^{2-}$ which is only a rather weak reductant and completely stable in most solvents including water. It belongs to a class of cluster anions with the general composition $B_nH_n^{2-}$ [9]. Such polyhedral *closo*-boranes are characterized by remarkable properties. These very stable clusters have highly symmetrical structures and are regarded as three-dimensional aromatic species. Moreover, calculations on the icosahedral $B_{12}H_{12}^{2-}$ anion have led to the conclusion that the extra charge of −2 is localized mainly on the surface of this anion [10]. This should facilitate an OSCT interaction with oxidizing cations. Indeed, the electronic spectrum of the ion pair

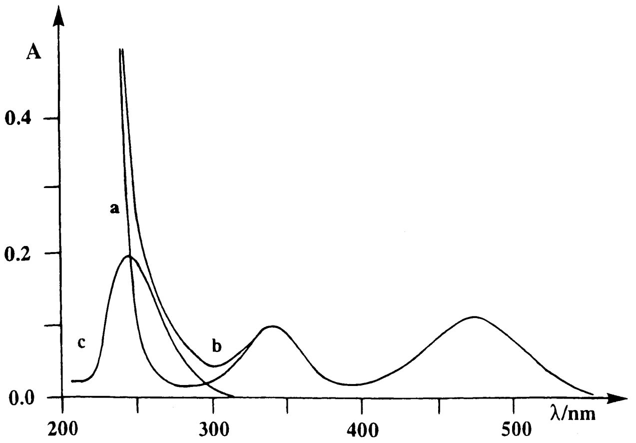
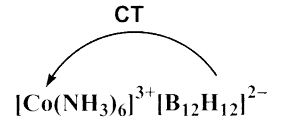


Fig. 1. Electronic absorption spectra of aqueous 4.08×10^{-3} M $[Co(NH_3)_6]Cl_3$ and 4.08×10^{-3} M $K_2[B_{12}H_{12}]$ as separate solutions (a), as a mixture (b), and the difference spectrum (c = b − a) at room temperature, 1-cm tandem cell.

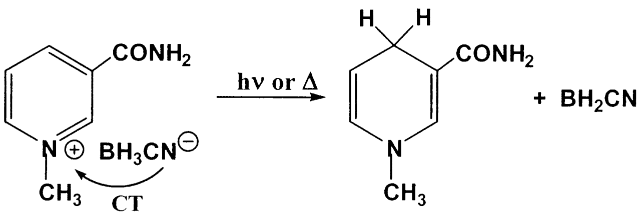


$$\overset{\mathrm{CT}}{[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}}$$

revealed the presence of a new absorption band at $\lambda_{max} = 250$ nm (Fig. 1) which is assigned to the OSCT transition from $B_{12}H_{12}^{2-}$ to $[Co(NH_3)_6]^{3+}$ [11]. This band was analyzed according to the Hush model [12,13]. The energy of the absorption maximum is the sum of the reorganizational energy χ and the potential difference ΔE of both redox couples $[Co(NH_3)_6]^{3+/2+}$ and $B_{12}H_{12}^{2-/-}$. With $\Delta E = 2.58$ V the reorganizational energy is approximately $\chi = 19\,200$ cm^{-1} [11] assuming that the difference of work terms for this OSCT couple is zero. This large value is attributed to the considerable structural changes which are associated with the reduction of $[Co(NH_3)_6]^{3+}$ and the oxidation of $B_{12}H_{12}^{2-}$ [11]. The OSCT excitation of the ion pair leads to the reduction of Co(III) with $\phi = 0.03$ at $\lambda_{irr} = 313$ nm. It is suggested that the photolysis proceeds according to the equation

$$2\{[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}\}\xrightarrow{h\nu}2Co^{2+}+11NH_3+NH_4^+ + [B_{24}H_{23}]^{3-} \qquad (1)$$

In a subsequent study it has been shown that BH_3CN^- can be also used as an OSCT donor. While BH_3CN^- is much more reactive than $B_{12}H_{12}^{2-}$ it is much less than BH_4^-. Cyanoboro-hydride is rather stable in aqueous solution and reacts much slower as reductant in comparison to BH_4^- [14]. As donor/acceptor system of particular interest we have investigated the ion pair $MNA^+BH_3CN^-$ with MNA^+ = 1-methyl nicotinamide cation (or 1-methyl-3-carbamoyl pyridinium cation) [15]:



MNA^+ represents the redox active site of NAD^+ (or $NADP^+$). In natural photosynthesis it is reduced finally to the dihydropyridine NADH (or NADPH) as energy

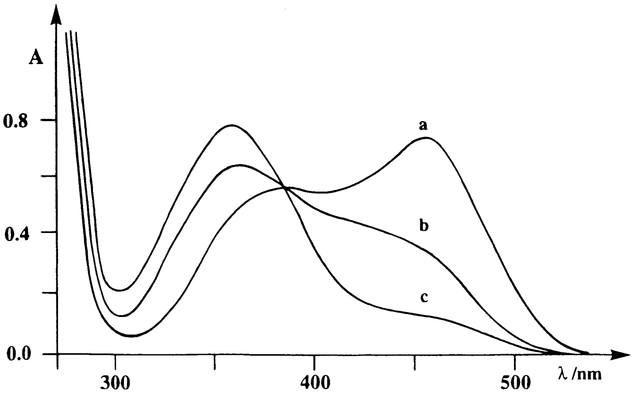


Fig. 2. Spectral changes during the thermal reaction of a mixture of 1.31×10^{-2} M $\mathrm{MNA^+ClO_4^-}$ and 1.31×10^{-2} M $\mathrm{Na^+BH_3CN^-}$ in $\mathrm{H_2O}$ at 3 °C after 4 (a), 10 (b) and 20 (c) s; 1 cm cell.

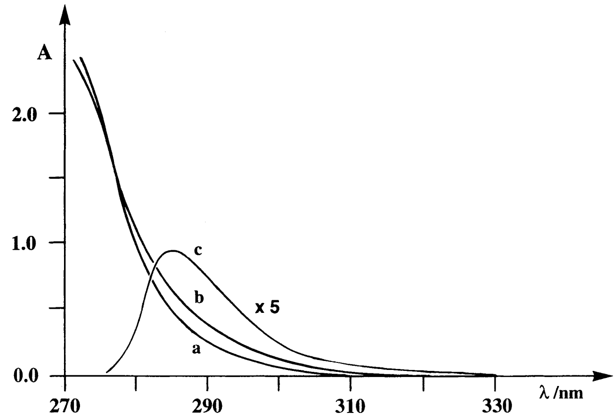


Fig. 3. Electronic absorption spectra of 2.8×10^{-2} M $\mathrm{[Ph_2I]Cl}$ (a), an equimolar (2.8×10^{-2} M) mixture of $\mathrm{[Ph_2I]Cl}$ and $\mathrm{Na[BH_3CN]}$ (b), and the difference spectrum (c = b − a) in $\mathrm{CH_3OH}$ at room temperature, 1-cm tandem cell.

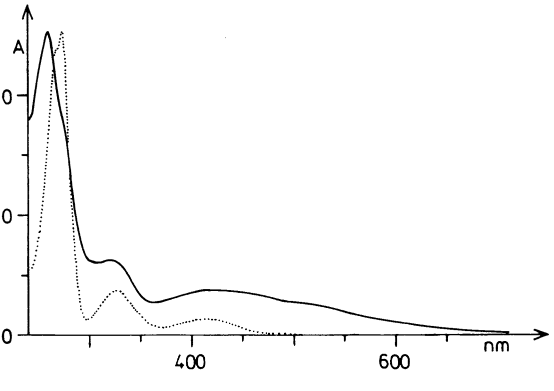


Fig. 4. Electronic absorption spectra of 8.28×10^{-5} M phenanthrenequinone (···) and 5.65×10^{-5} M $(i\text{-}\mathrm{C_3H_7C_5H_4})_2\mathrm{WH_2} \cdot$ 9,10-phenanthrenequinone (—) in $\mathrm{CH_2Cl_2}$ at room temperature under argon, 1 cm cell.

rich product. Generally, pyridinium cations can be reduced to the corresponding dihydropyridines by hydride transfer [16,17]. Since borohydrides are typical hydride transfer reagents they are applied widely for the reduction of pyridinium cations [18,19]. This happens also as a thermal process in the ion pair $\mathrm{MNA^+}$ $\mathrm{BH_3CN^-}$ at room temperature [15]. The intermediate formation of the ion pair is recognized by the appearance of an orange color. The accompanying new absorptions at $\lambda_{\max} = 453$ nm (Fig. 2) is assigned to an OSCT transition from $\mathrm{BH_3CN^-}$ to $\mathrm{MNA^+}$. When the solution is cooled down to − 77 °C the ion pair is thermally stable but can be converted to the dihydropyridine MNAH by OSCT excitation ($\lambda_{\mathrm{irr}} > 240$ nm).

The ion pair $\mathrm{Ph_2I^+BH_3CN^-}$ is a further example with $\mathrm{BH_3CN^-}$ as donor [20]. The OSCT absorption (Fig. 3) appears at $\lambda_{\max} = 285$ nm. $\mathrm{Ph_2I^+}$ as CT acceptor has been used before [6,21]. OSCT excitation of $\mathrm{Ph_2I^+BH_3CN^-}$ ($\lambda_{\mathrm{irr}} > 300$ nm) leads to a photolysis [20]. A preliminary analysis of the photoproducts is consistent with the following equation

$$\mathrm{Ph_2I^+BH_3CN^-} \xrightarrow{h\nu} \mathrm{C_6H_6} + \mathrm{C_6H_5I} + \mathrm{BH_2CN} \qquad (2)$$

This reaction scheme is quite reasonable since the photochemical reductive fragmentation of $\mathrm{Ph_2I^+}$ has been previously observed [6,21].

In this context it is rather interesting that $\mathrm{H^-}$ transfer can be also achieved by OSCT excitation in quite different systems. An intriguing example involves a metal hydride complex as donor [22,23]:

$$(i\text{-}\mathrm{C_3H_7C_5H_4})_2\mathrm{WH_2} \cdot \text{9,10-phenanthrenequinone} \xrightarrow{h\nu}$$
$$(i\text{-}\mathrm{C_3H_7C_5H_4})_2\mathrm{W} + \text{9,10-phenanthrenediol} \qquad (3)$$

In this case the CT interaction ($\lambda_{\max} = 530$ nm, Fig. 4) takes place between neutral molecules. Moreover, reduction of the quinone does not occur by hydride transfer but proceeds by accepting a $\mathrm{H_2}$ molecule from the hydride complex [23].

Hydride transfer can be also viewed as a two-electron/one-proton transfer. In this case a hydridic donor is not required. For example, the ion pair $\mathrm{MNA^+}$ $\mathrm{[Fe(CN)_6]^{4-}}$ shows a new absorption at $\lambda_{\max} = 392$ nm which is assigned to an OSCT transition from $\mathrm{[Fe(CN)_6]^{4-}}$ to $\mathrm{MNA^+}$ [24]. Upon OSCT excitation ($\lambda_{\mathrm{irr}} = 436$ nm) $\mathrm{MNA^+}$ is reduced to MNAH with $\phi = 0.002$. The overall reaction proceeds according to the equation

$$\mathrm{MNA^+} + 2[\mathrm{Fe^{II}(CN)_6}]^{4-} + \mathrm{H^+}$$
$$\rightarrow \mathrm{MNAH} + 2[\mathrm{Fe^{III}(CN)_6}]^{3-} \qquad (4)$$

OSCT excitation leads to the radical pair $\mathrm{MNA^{+\bullet}}$/ $[\mathrm{Fe^{II}(CN)_6}]^{3-}$. $\mathrm{MNA^\bullet}$ is further reduced thermally by $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ which is present in excess. Finally, proton uptake yields MNAH.

3. Carbanionic donor anions

Generally, carbanions $\mathrm{R^-}$ are strong reductants but also powerful nucleophiles which undergo a facile reac-

Table 1
OSCT absorptions of aqueous $PQ^{2+}X^{n-}$

X^{n-}	SCN^-	$S_2O_3^{2-}$	SbS_4^{3-}	PO_3S^{3-}	$C(OEt)S_2^-$	$P(OEt)_2S_2^-$ [a]	WS_4^{2-}
λ_{max} (nm)	329	341	370	376	394	400	431
ε ($l\ mol^{-1}\ cm^{-1}$)	44	47	60	55	32	–	60

[a] In CH_3CN.

tion with electrophiles including protons. For example, the complex $[(\eta^7\text{-}C_7H_7)Mo^0(CO)_3]^+$ which contains the tropylium cation as ligand rapidly adds carbanions (e.g. from Li–R) to generate the cycloheptatriene $R\text{–}C_7H_7$ as a neutral ligand [25,26]. However, in analogy to hydride the nucleophilicity of R^- is attenuated when it is added to BR_3. Since the resulting anion BR_4^- still retains—at least partially—the reducing properties of R^- it can be utilized as OSCT donor [6,27]. The ion pair $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]^+BPh_4^-$ shows a new absorption band at $\lambda_{max} = 370$ nm which is assigned to the OSCT transition from BPh_4^- to the complex cation [28]. OSCT excitation ($\lambda_{irr} > 390$ nm) leads to a photolysis according to the equation

$$[(\eta^7\text{-}C_7H_7)Mo(CO)_3]^+BPh_4^- \xrightarrow{h\nu} (\eta^6\text{-}C_7H_4Ph)Mo(CO)_3 + BPh_3 \quad (5)$$

CT excitation is associated with the formation of the radical pair $[C_7H_7Mo(CO)_3]/BPh_4$. BPh_4 undergoes a fragmentation to BPh_3 and a phenyl radical which finally couples with the complex radical to yield the phenylcycloheptatriene complex. In summary, the photoreactivity of a redoxactive ion pair containing BPh_4^- was used to covalently add the phenyl anion to a suitable cation.

4. Sulfidic donor anions

In analogy to H^- and R^-, sulfide is not only reducing but also a strong nucleophile which prevents its application as OSCT donor in ion pairs. Again, S^{2-} can be incorporated in other anions in order to obtain sulfidic anions which are reducing but not nucleophilic. Generally, anions such as SO_4^{2-}, PO_4^{3-}, SbO_4^{3-} and WO_4^{2-} are not reductants but weak oxidants owing to the high oxidation states of their central atoms. However, they become reducing if oxide substituents are replaced by sulfide, e.g.

$S_2O_3^{2-}$, PO_3S^{3-}, SbS_4^{3-} and WS_4^{2-}.

The donor character of sulfide in such anions is also documented by the low energies of LMCT transitions of SbS_4^{3-} ($\lambda_{max} = 285$ nm) [29] and WS_4^{2-} ($\lambda_{max} = 392$ nm) [30,31].

The ion pairs $[Ru(NH_3)_6]^{3+}S_2O_3^{2-}$ and $[Ru(NH_3)_6]^{3+}PO_3S^{3-}$ show OSCT absorptions at $\lambda_{max} =$ 412 and 486 nm, respectively [32]. When *N*,*N′*-dimethyl-4,4′-bipyridinium^{2+} (paraquat^{2+}, PQ^{2+} or methylviologen) is used as an acceptor cation, ion pairs with a variety of sulfidic anions are formed. They are all characterized by OSCT absorptions (Table 1, Fig. 5) [32] which in most cases are responsible for the colors of these ion pairs. The energies of these OSCT bands can be used to establish a series of sulfidic anions with increasing CT donor strength:

$$SCN^- < S_2O_3^{2-} < SbS_4^{3-} < PO_3S^{3-} < P(OEt)_2S_2^- < WS_4^{2-}.$$

This series might correspond to Jørgensen's optical electronegativities [1]. For reducing ligands they are derived from the energies of LMCT transitions. Unfortunately, optical electronegativities are often unknown because appropriate complexes of such ligands have not been prepared or their absorption spectra have not been measured or analyzed. In another model which has been introduced recently by Lever a ligand electrochemical series was derived from redox potentials of a large number of metal complexes [33]. However, the determination of OSCT energies offers a simple alternative to evaluate the donor strength of anions irrespective of their coordinating ability. Of course, these OSCT energies do not directly correlate with electrochemical potentials owing to contributions by reorganization energies [34].

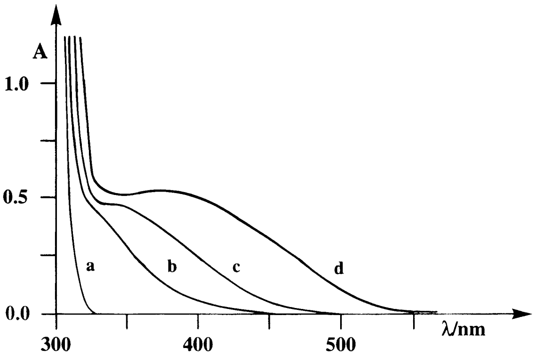


Fig. 5. Electronic absorption spectra of aqueous 1.01×10^{-2} M $PQCl_2$ (a) and equimolar (1.01×10^{-2} M) mixtures of $PQCl_2$ and NaSCN (b), $Na_2S_2O_3$ (c), and Na_3PO_3S (d) in water at room temperature, 1-cm cell.

5. Peroxidic donor anions

Hydrogen peroxide is a reductant as well as an oxidant. Accordingly, it tends to dismutate to water and oxygen. This ambivalence is also documented by the electronic spectra and photochemistry of transition metal complexes with peroxide as ligand. In combination with reducing and oxidizing metals low-energy MLCT [35,36] and LMCT [37,38] transitions, respectively, occur. While MLCT excitation leads to the reduction of peroxide to water, LMCT transitions induce the oxidation to oxygen. The application of O_2^{2-} as a CT donor or acceptor could be extended considerably if it participates in OSCT. Again, peroxide is a strong nucleophile which does not form suitable ion pairs in solution. However, peroxide can be replaced by peroxidic anions such as peroxoborate and peroxodisulfate which are hardly nucleophilic. Peroxoborate (or perborate) is available as $NaBO_3 \times H_2O$. In aqueous solution $[B_2(O_2)_2(OH)_4]^{2-}$ and other anions with boron-peroxo moieties are present. These various species are summarized as BO_3^- [39].

The ion pairs of BO_3^- and the oxidizing cations $[Co(NH_3)_6]^{3+}$, PQ^{2+} and $[Ru(NH_3)_6]^{3+}$ in water show OSCT transitions at $\lambda_{max} = 283$, 388 and 402 nm, respectively [39]. This red shift agrees qualitatively with the increasing oxidation strength of the cations. Of course, these OSCT energies may not correlate directly with electrochemical data owing to the contributions by reorganization energies [34].

Peroxodisulfate is also suitable as a peroxidic OSCT donor. The ion pair $[Ru(NH_3)_6]^{3+}S_2O_8^{2-}$ displays an OSCT absorption at $\lambda_{max} = 461$ nm ($\varepsilon = 4$) [40]. While these observations have shown that peroxidic anions are versatile OSCT donors their use as photoreductants for oxidizing cations has not yet been studied but should be exploited in future applications.

6. Conclusion and outlook

Ion pairs which consist of an oxidizing cation and a reducing anion are characterized by an OSCT absorption. OSCT excitation frequently leads to a photolysis which is not observed for the separate constituents of the ion pairs. Unfortunately, various important reductants such as H^-, R^- (carbanions), S^{2-} and O_2^{2-} are not suitable as donor anions owing to their strong nucleophilicity. However, this disadvantage can be circumvented if they are incorporated in other anions, e.g. BH_3CN^- for H^-, BPh_4^- for Ph^-, PO_3S^{3-} for S^{2-}, and BO_3^- for O_2^{2-}.

As an extension of this concept oxidizing cations which are strong electrophiles such as carbenium ions R^+ can be also applied in a protected form (e.g. NR_4^+). Accordingly, the non-existent ion pair R^+R^- might be replaced by $NR_4^+BR_4^-$. Indeed, $[N(n\text{-butyl})_4]^+[B(n\text{-butyl})_4]^-$ has been shown recently to display an OSCT absorption ($\lambda_{max} = 306$ nm) [41]. OSCT excitation leads to the formation of octane which may be formed by the coupling of two *n*-butyl radicals. An electron-accepting cation of particular importance would be a proton. However, preliminary attempts to examine ion pairs with NH_4^+ as less reactive substitutes for H^+ were not yet successful.

Acknowledgements

Support for this research by the Fonds der Chemischen Industrie is gratefully acknowledged.

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