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Coordination Chemistry Reviews
159 (1997) 257–270

COORDINATION CHEMISTRY REVIEWS

Optical and photoinduced electron transfer in ion pairs of coordination compounds

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Received 22 December 1995

Contents

Abstract

Electrostatic attraction between charged coordination compounds and oppositely charged counter ions in solution leads to ion pairing. Although ion pairs are loosely bound species, their spectroscopic and photochemical properties may markedly differ from those of the individual components. Upon favourable mutual energetic positions of the redox orbitals additional ion pair charge-transfer (IPCT) optical transitions may be observed. The various contributions to the energy of the IPCT band absorption maximum and an increment system for the prediction of the position of these maxima are discussed. Depending on the choice of the components and the irradiation wavelength, ion pairs may undergo energy transfer, photoinduced electron transfer and optical electron transfer respectively. Fast subsequent thermal reactions have to compete with back electron transfer in order to achieve high yields of permanent photo-redox products. Mechanistic aspects of the product formation are discussed with respect to ion pairs of, for example, cobalt(III)amines. Ion pairs of coordination compounds may find use as photoinitiators for microimaging and curing applications, as well as photocatalysts for selective organic synthesis. © 1997 Elsevier Science S.A.

Keywords: Coordination compound; Optical electron transfer; Photoinduced electron transfer; IPCT optical transitions

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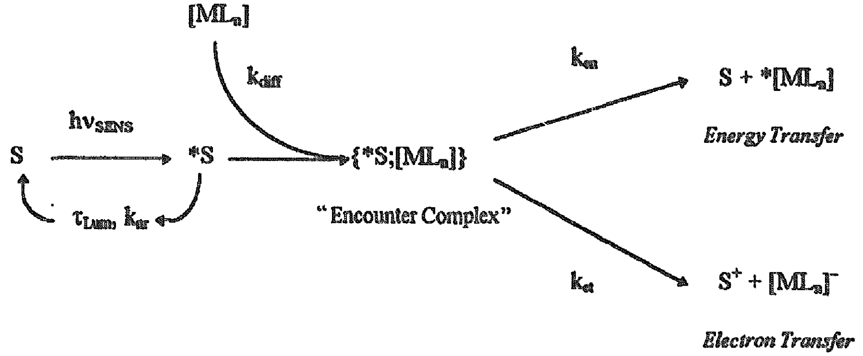
PII S0010-8545(96)01288-X

1. Introduction

Light-induced electron-transfer processes involving metal complexes frequently lead to dramatic alterations of the chemical properties of these compounds, e.g. like redox properties, kinetic stability, catalytic activity, and acid–base properties, which provide the basis for the formation of permanent photoproducts [1–4]. Therefore, such processes are of potential interest with respect to the design of photocatalytic systems for unconventional information recording materials, solar energy conversion and the generation of catalysts in organic synthesis [4–6].

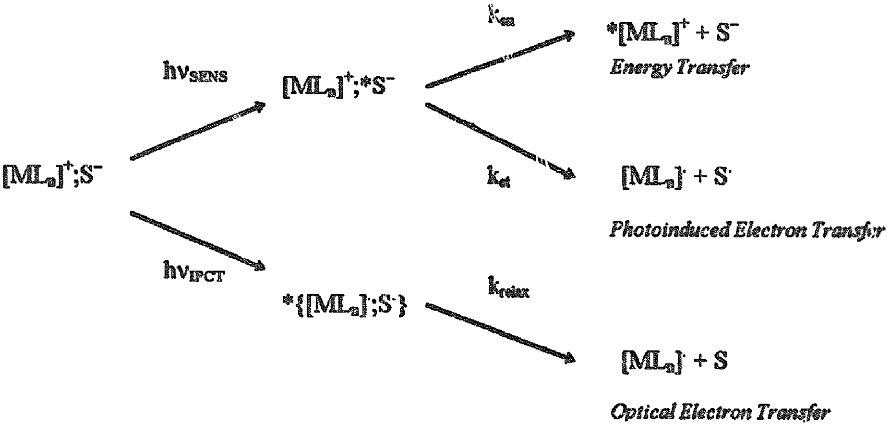
In simple systems, consisting of a light-sensitive coordination compound and an appropriate substrate in a suitable solvent, short excited-state lifetimes and back electron transfer may dramatically decrease the efficiency of product formation. In addition, owing to the absorption characteristics of the complex and the substrate, the light of a given source may, respectively, either be not or insufficiently absorbed by the potential photocatalyst [7]. Thus, a long-wavelength spectral sensitization of the coordination compound is required. This situation is illustrated by Scheme 1, where S is a sensitizer (e.g. a dye) which is able to absorb light of wavelengths longer than the complex $[ML_n]$ itself.



Scheme 1.

Since the three functional components of light-induced electron transfer, i.e. donor, acceptor and light-absorbing chromophore, very often are not contained in one molecular entity, the efficiency of sensitization is markedly reduced by diffusion control (k_{diff}) of the formation of encounter complexes. This disadvantage of bimolecular photoreactions can be overcome by static sensitization, i.e. under conditions where the functional components already form a relatively stable (supra)molecular entity prior to light absorption.

Coordination compounds frequently are charged species. Thus, ion pairing between oppositely charged complex and sensitizer ions renders an attractive opportunity to create the conditions for static sensitization, Scheme 2. Ion pairing combines the advantages of the uncomplicated synthesis of the supramolecular species, when compared with the introduction of sensitizer molecules as a ligand into the first coordination sphere of a metal complex, with those of a wide variability of the photochemical, photophysical and redox properties of the individual components [8,9]. Furthermore, upon a favourable energetic position of the redox orbitals, long-wavelength charge-transfer transitions between the ions, termed ion pair charge-transfer (IPCT) transitions, may occur. Depending on the choice of the components and the irradiation wavelength, ion pairs may undergo energy transfer (leading to the population of non-spectroscopic charge-transfer excited states), photoinduced electron transfer (as a thermal reaction from a locally excited state of the sensitizer), and optical electron transfer.



Scheme 2.

In this article, we will concentrate on the spectroscopy and photochemistry of ion pairs involving coordinatively saturated and kinetically inert Werner-type complexes mainly in aqueous solution. Earlier work on this subject has been reviewed elsewhere [9–13], covering the literature until ca. 1989. For comprehensive reviews on ion pairs in non-aqueous solutions [13,14], ion pairs formed by labile metal aquo complexes [15] and on thermal electron transfer reactions involving ion pairs as precursors [11,16] the reader is referred to a number of monographs and review articles.

2. IPCT optical transitions

In addition to electrostatic attractive forces and hydrogen bonding interactions, and depending on the relative energies of the highest occupied and lowest unoccupied orbitals respectively, ion pairing may lead to electronic interactions between the components that result in novel electronic states within the ion pair [9,17]. The population of these electronic states may bring about additional spectroscopic, photophysical and photochemical properties of the ion paired with respect to the free mobile species, while the individual properties of the components remain essentially unaltered. Owing to the weakness of the electronic coupling, the energies of these novel electronic states are mainly determined by the difference in redox potentials of the participating ions. If these differences are small, additional IPCT transitions which correspond to an electron transfer from the donor ion to the acceptor ion may show up in the ultraviolet, visible or near infrared spectral region, Fig. 1. IPCT behaviour of a coordination compound has been observed for the first time by Linhard [19] in the aqueous $\{[Co(NH_3)_6]^{3+};I^-\}$ system.

IPCT transitions represent a special case of the more general outer-sphere charge-transfer (OSCT) or second-sphere charge-transfer (SSCT) phenomena [9,17,20]. OSCT transitions have been observed between charged metal complexes and neutral donors [21] and acceptors [12], between uncharged coordination compounds [12] and even between identically charged complex ions in solution [22–24]. Owing to the lack of electrostatic attractive forces between the components, however, the formation constants of the absorbing species are much lower than those of ion pairs of oppositely charged species.

A model for the description of the energetic changes upon IPCT excitation of an ion pair $\{A^+;D^-\}$ has been introduced by Cannon [17]. Here, and in the following, the superscripts 'plus' and 'dot' and 'minus' are used to symbolize the oxidation states of the donor D and acceptor A respectively, but not necessarily the charge type. Based on several assumptions, Eq. (1) has been deduced for the free energy change ΔG_{IPCT} of the ion pair system due to IPCT excitation.

$$\Delta G_{IPCT} = h\nu_{max,IPCT} = \Delta E_{IPCT} = \Delta G_E - \Delta G_W + \Delta G_{W'} + \Delta G_{FC} \quad (1)$$

The redox asymmetry ΔG_E is related to the redox potentials E^0 of the components

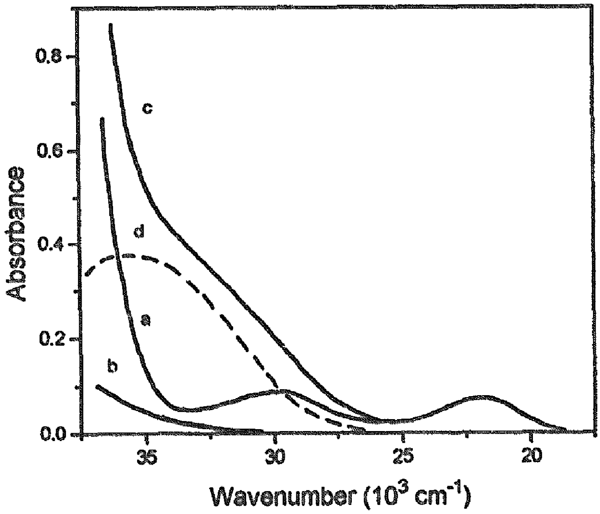


Fig. 1. IPCT in the aqueous $\{[Co(tacn)_2]^{3+};I^-\}$ system: (1) $[Co(tacn)_2](ClO_4)_3$; (2) KI; (3) a mixture of solutions (1) and (2); (4) difference spectrum (3)−[(1)+(2)]. For details see Ref. [18].

by Eq. (2), where F is the Faraday constant.

$$\Delta G_E = F[E^0(D^{\cdot}/D^-) - E^0(A^+/A^{\cdot})] \qquad (2)$$

The work terms ΔG_W and $\Delta G_{W''}$ for the precursor and the successor pair formation respectively, can be estimated using the Eigen–Fuoss equation [25]. In aqueous solution, however, the difference between these values has only minor importance for ΔG_{IPCT}. The Franck–Condon, or reorganization free energy, ΔG_{FC} may be further split into inner- and outer-sphere contributions. Various approaches have been developed in order to calculate ΔG_{FC} from structural data of the components in the oxidized and reduced forms [17,26,27]. The predicted dependence of ΔG_{FC} on the so-called Pekar parameter $(D_{op}^{-1} - D_s^{-1})$, where D_{op} and D_s are the optical and static dielectric constants of the bulk solvent respectively, has been confirmed for several ion pairs by a multi-parameter regressional analysis [28] which also considered the solvent effect on ΔG_E.

It should be pointed out that Eq. (1) holds true only for the lowest-energy IPCT transition in a given system. If the degeneracy of multiple IPCT excited states is lifted by spin–orbit splitting, the observed IPCT band envelope may be a result of the superposition of several individual bands with different absorption maxima. For example, such a behaviour, accompanied by band-broadening, is observed for ion pairs of hexacyanoosmate(II) [29]. Ion pairs of halides like iodide show up two well-resolved IPCT transitions, corresponding to the population of the $^2P_{1/2}$ and $^2P_{3/2}$ states of the iodine atom [30]. However, an IPCT transition described by Eq. (1) is not necessarily observable since it might be spin-forbidden. This is the case for ion pairs involving cobalt(III)amines (see below).

The application of Eq. (1) in principle would allow for the calculation of ΔG_{IPCT} for any ion pair combination. Unfortunately, the complete set of structural and electrochemical data required is only rarely available. However, upon variation of the cationic component in the ion pairs of a series of anions for example, a linear relation between the IPCT absorption maxima is observed (Fig. 2).

Based on this observation, an increment system for the prediction of ΔG_{IPCT} of as yet unexplored ion pairs has been proposed [31]. Within a certain limit ($\pm 2500\ \mathrm{cm}^{-1}$) the IPCT absorption maximum of an ion pair $\{A^+;D^-\}$ may be estimated according to Eq. (3). Selected values of acceptor, $I(A^+)$, and donor, $I(D^-)$, ion increments are given in Tables 1 and 2.

$$\Delta G_{IPCT}\{A^+;D^-\} = I(A^+) + I(D^-) \qquad (3)$$

For a number of structurally very different components within the acceptor and donor ion series respectively, there is a rough correlation [31] between the values of the ion increments and the redox potentials. This may be interpreted in terms of a major contribution of variations in ΔG_E to those in ΔG_{IPCT}, Eqs. (1) and (2). A strong deviation from this relationship indicates large individual contributions to ΔG_{FC}, i.e. dramatic structural changes of the component as a result of optical electron transfer. This is the case for diphenyliodonium ions [37] and cobalt(III)amine complexes [26,30,35] as acceptors. There is, however, another

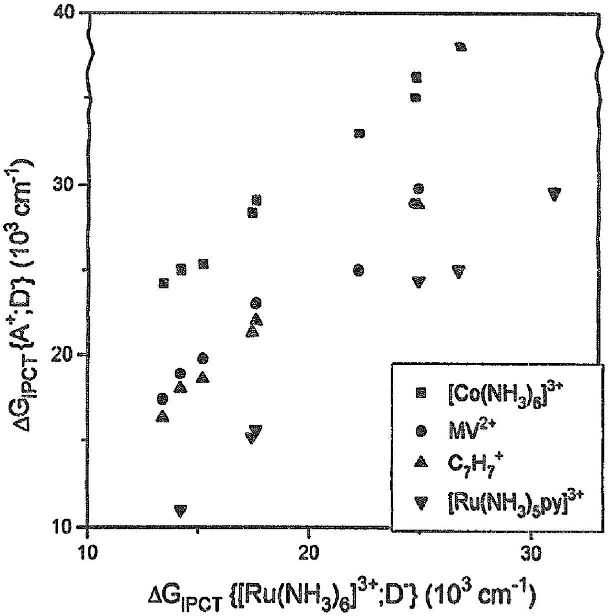


Fig. 2. Plot of ΔG_{IPCT} for ion pairs of several cations vs. ΔG_{IPCT} for hexammineruthenium(III) ion pairs with the same anions D^- (from left to right: $[W(CN)_8]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Mo(CN)_8]^{4-}$, $[Os(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, $[Fe(CN)_5CO]^{3-}$, $SeCN^-$, I^-, SCN^- Br^-; data taken from Ref. [13]).

peculiarity of the latter class of compounds. The electrochemically determined reduction potentials correspond to the transition from low-spin Co^{III} (t_{2g}^6) to high-spin Co^{II} ($t_{2g}^5e_g^2$). An IPCT transition leading to the primary formation of the thermodynamically stable high-spin Co^{II} would be a three-electron process and spectroscopically forbidden. The observed IPCT transitions in ion pairs of cobalt(III)amines and -diimines, however, correspond to a one-electron process leading to the formation of low-spin Co^{II} ($t_{2g}^6e_g^1$). Thus, it is no surprise that the ΔG_{IPCT} values for ion pairs of cobalt(III) complexes with iodide ions do not show any correlation with the high-spin (ground state) reduction potentials of the cations, Fig. 3(a), but increase linearly with decreasing low-spin reduction potentials, Fig. 3(b). The latter quantities have been calculated for a number of cobalt(III) complexes by application of ligand-field theoretical arguments [26,38,35].

The extent of electronic coupling between the components of an ion pair, quantified by the matrix element H_{AD}, can be estimated from the integrated absorption intensity of the IPCT band according to Eq. (4) [39], where R is the distance between the redox centres and g is the multiplicity of the excited states concerned.

$$H_{AD}^2 = 4.24\times10^{-4}\,\frac{\Delta\tilde{\nu}_{1/2}\epsilon_{max}\tilde{\nu}_{max}}{R^2 g} \qquad (4)$$

Such calculations have been performed for a series of ion pairs $\{[Ru(NH_3)_5L]^{3+};[M(CN)_6]^{4-}\}$, where L is a heterocyclic ligand and M = Fe, Ru

Table 1
Increments $I(A^+)$ and redox potentials $E^0(A^+/A^{\cdot})$ for selected acceptor ions A^+ in aqueous solution[a]

A^+	$I(A^+)$ (10^3 cm^{-1})	E^0 (V vs. NHE)
$[Ru(en)_3]^{3+}$	−7.5	+0.18
$[Ru(NH_3)_5H_2O]^{3+}$	−4.1[b]	—
$[Ru(NH_3)_6]^{3+}$	−4.0	+0.05
$[Ru(NH_3)_5Cl]^{2+}$	−2.4	−0.04
$C_7H_7^+$	0.0	−0.19
MV^{2+}	0.9	−0.42
$[Eu(2.2.1)]^{3+}$	0.9	−0.18
4,4'-$bpyH_2^{2+}$	1.9[d]	—
$[Rh(bpy)_3]^{3+}$	2.8	−0.86
$[Co(bpy)_3]^{3+}$	2.9	+0.31/+0.01[e]
$[Os(NH_3)_5H_2O]^{3+}$	3.0[b]	—
$[Os(NH_3)_5Cl]^{2+}$	4.8	−0.56
$[Co(sep)]^{3+}$	5.0	−0.3/−0.47[e]
$[Co(chxn)_3]^{3+}$	5.9	−0.1/−0.56[e]
$[Co(pn)_3]^{3+}$	6.3	−0.1/−0.52[e]
$[Co(tacn)_2]^{3+}$	6.3	−0.41/−0.48[e]
p-MeO–$C_6H_4N_2^+$	6.7	—
$[Co(en)_3]^{3+}$	7.3	−0.18/−0.56[e]
$[Co(NH_3)_6]^{3+}$	7.4	+0.08/−0.48[e]
$[Pt(NH_3)_5Cl]^{2+}$	8.1	—
Ph_2I^+	8.9	−0.5
$[Cr(en)_3]^{3+}$	11.2[c]	—
$[Cr(NH_3)_6]^{3+}$	13.0[c]	—

[a] Based on data from Refs. [13,31] unless otherwise indicated; [b] from Ref. [32]; [c] from Ref. [33]; [d] from Ref. [34]; [e] low-spin reduction potentials [35], see text.

and Os [29]. The values of H_{AD} obtained appear to be sufficiently high to ensure a nearly adiabatic nature of the corresponding thermal electron transfer reactions. From more recent investigations on ion pairs $\{[CoL_6]^{3+};I^-\}$, where L is an amine or α-diimine ligand [18], it was concluded that the extent of electronic interaction between the redox centres is almost constant within a range of $R = 540$–910 pm. An exponential decay of H_{AD} on increasing R, however, would have been expected from electron transfer theory [40,41]. Thus, the need for further work in this field is indicated.

Finally it should be pointed out that the overwhelming majority of IPCT transitions observed up to now correspond to the transfer of an electron from an anion to a cation. Very recently, first examples of IPCT transitions in the converse direction have been reported [32] for ion pairs $\{[M(NH_3)_5L]^{3+};[Fe(CN)_6]^{3-}\}$, where M = Ru, Os and L = NH_3 or H_2O.

3. Photo-redox reactions of ion pairs

Three general pathways of photo-redox reactions of ion pairs have been depicted in Scheme 2 (see Section 1). Interestingly, intramolecular electron transfer in a

Table 2
Increments $I(D^-)$ and redox potentials $E^0(D^\bullet/D^-)$ for selected donor ions D^- in aqueous solution[a]

D^-	$I(D^-)$ (10^3 cm^{-1})	E^0 (V *vs.* NHE)
$[W(CN)_8]^{4-}$	16.3	0.46
$[Fe(CN)_6]^{4-}$	18.0	0.36
$[Mn(CN)_5NO]^{3-}$	18.4	0.66
$[Mo(CN)_8]^{4-}$	18.6	0.73
$[Os(CN)_6]^{4-}$	21.5	0.63
$[Ru(CN)_6]^{4-}$	22.0	0.86
NO_2^-	26.7[b]	1.13
$SeCN^-$	26.7	1.27
N_3^-	28.1[b]	1.27
I^-	28.9/35.5[c]	1.33
SCN^-	31.1	1.66
Br^-	31.6/33.8[c]	1.90
$RCOO^-$	31–33[b]	2.0–2.4
$C_2O_4^{2-}$	31.4[b]	2.1
OCN^-	32.1[b]	2.18
Cl^-	38.0	2.49
$[Rh(CN)_6]^{3-}$	38.0	—

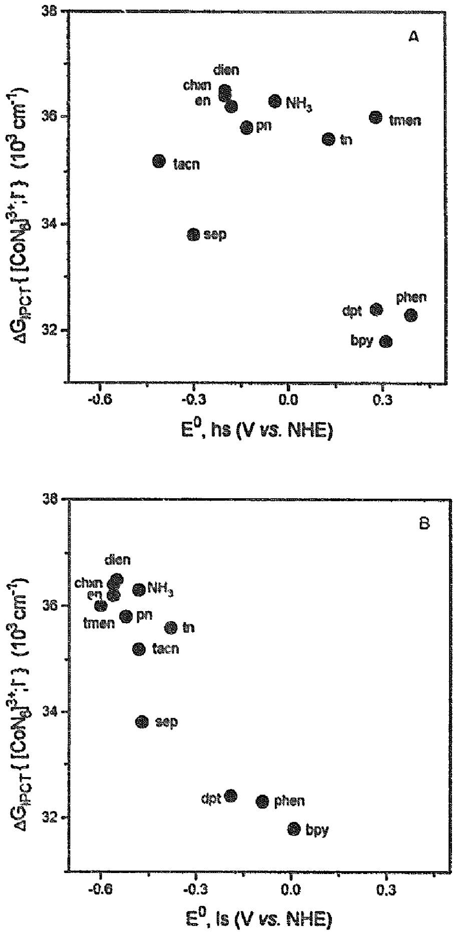
[a] Based on data from Refs. [13,31] unless otherwise indicated; [b] from Ref. [36], R = alkyl or aryl; [c] transitions leading to the halogen atoms in their lower $^2P_{3/2}$ and upper $^2P_{1/2}$ states, cf. [30].

coordination compound induced by energy transfer from the counter ion excited state has so far not been reported. Both the inner-sphere analogue of such a process and the sensitization of intramolecular redox reactions by neutral sensitizers, however, have been known for a long time [42].

Optical electron transfer by irradiation into the IPCT absorption band of an ion pair $\{A^+;D^-\}$ (Scheme 3) primarily leads to the successor pair $\{A^\bullet;D^\bullet\}_{FC}$ in the Franck–Condon excited state. The rate of relaxation of $\{A^\bullet;D^\bullet\}_{FC}$ into its thermally equilibrated ground state $\{A^\bullet;D^\bullet\}$ is limited by the dielectric relaxation of the solvent [43], which is slow compared with in[illegible] the [illegible]. Radiationless deactivation into the ion pair ground state may compete with relaxation [44], but the energetic requirements are rarely met [11]. In general, the efficiency of relaxation after IPCT excitation may be assumed to be close to unity.

The relaxed successor pair $\{A^\bullet;D^\bullet\}$ can react in different ways. The precursor ion pair $\{A^+;D^-\}$ may be regenerated either by luminescence (k_{lum}) [45] or by thermal back electron transfer (k_{back}). The solvated free species $A^\bullet$ and $D^\bullet$ formed by diffusive solvent cage escape (k_{ce}) can undergo subsequent thermal reactions from the bulk solution ($k_{p,bulk}$). Furthermore, permanent product formation may occur by very rapid in-cage decay of the successor pair components ($k_{p,cage}$).

If rapid subsequent thermal reactions of $A^\bullet$ and $D^\bullet$ respectively, prevent the recombination of the successor pair from the bulk solution (k_{diff}), the cage escape efficiency, $\eta_{ce} = k_{ce}/(k_{ce} + k_{p,cage} + k_{back} + k_{lum})$, should be related to the observable quantum yield of product formation Φ_p. Based on the assumption that k_{back} is limited by the dielectric relaxation of the solvent, its maximum value should not

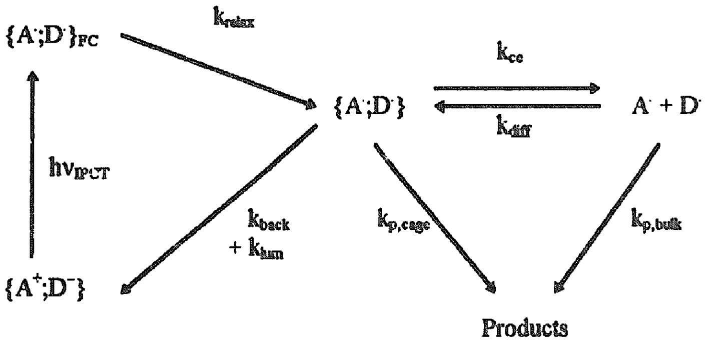


[illegible] ion pairs $\{[CoN_6]^{3+};I^-\}$, where $[CoN_6]^{3+}$ is a homoleptic amine or diimine complex, in aqueous solution vs. (a) the high-spin and (b) the low-spin reduction potential of the cations.

exceed $\tau_D^{-1} \approx 10^{11}\ s^{-1}$ (in water) [43]. In contrast, k_{ce} may be appropriately calculated from the radii of the successor pair components using the Eigen equation [25]. Hence, in the absence of both in-cage reactions and luminescent decay the cage-escape efficiency may be calculated according to Eq. (5).

$$\eta_{ce} = \frac{k_{ce}}{(k_{ce} + k_{back})} \tag{5}$$

In Table 3 the quantum yields of product formation upon IPCT excitation of a number of ion pairs in aqueous solution are compared with the calculated cage-escape efficiencies. Neglecting the fact that the individual quantum yields depend to a certain extent on the composition of the solution [48,49], there is a reasonable



Scheme 3.

Table 3
Calculated cage-escape efficiencies η_{ce} and experimental quantum yields Φ_{IPCT} for permanent product formation from ion pairs $\{A^+;D^-\}$ in aqueous solution upon IPCT excitation[a]

A^+	D^-	$r(A^\cdot)$ (pm)	$r(D^\cdot)$ (pm)	η_{ce}	Φ_{IPCT}
$[Co(NH_3)_6]^{3+}$	I^-	370	133	0.21	0.19
$[Co(NH_3)_6]^{3+}$	Cl^-	370	99	0.28	0.30
$[Rh(bpy)_3]^{3+}$	$[Fe(CN)_6]^{4-}$	700	430	1.7×10^{-3}	2.4×10^{-3}
$[Cr(en)_3]^{3+}$	$[Os(CN)_6]^{4-}$	400	450	1.2×10^{-3}	8×10^{-4}
Ph_2I^+	$[Fe(CN)_6]^{4-}$	350	430	5×10^{-2}	0.2[b]
$[Co(en)_3]^{3+}$	$[Ru(CN)_6]^{4-}$	400	450	1.2×10^{-3}	0.98
$[Co(sep)]^{3+}$	$C_2O_4^{2-}$	460	200	2.9×10^{-2}	0.44

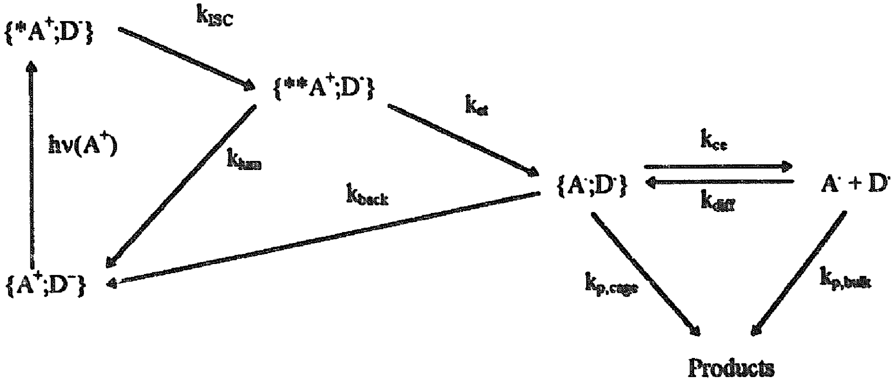
[a] Calculated according to Eq. (5); data taken from Refs. [12,13,38,46–49]. [b] In water–*tert*-butanol 50/50 (v/v).

agreement between the calculated and experimental values for the first four examples, supporting the validity of the kinetic model. The cage-escape yield seems to be limiting the quantum yield also for a number of similar ion pairs [10,12,13,47,50].

Values of $\Phi_p \gg \eta_{ce}$, as is the case for the last three entries in Table 3, indicate the rapid in-cage decay of the successor pair components. The high quantum yields upon IPCT photolysis of $\{Ph_2I^+;[M(CN)_x]^{4-}\}$ ion pairs has been attributed to the extremely short lifetime of the diphenyliodyl radical formed directly by optical electron transfer [37,51]. This interpretation is supported by the observation that the quantum yield remains almost constant upon increasing the solvent viscosity by more than 20 times [47]. Quantum yields close to unity have been measured upon IPCT photolysis of ion pairs $\{[Co(en)_3]^{3+};[M(CN)_6]^{4-}\}$ [38,52]. The very efficient formation of the photoproducts, $[(L)Co^{III}(en)_2\text{-}\mu\text{-}NC\text{–}M^{II}(CN)_5]^{n-}$ ($L = Cl^-$, H_2O or $[M(CN)_6]^{4-}$), can be attributed to rapid in-cage substitutional processes involving the primarily formed (see Section 2) kinetically labile low-spin $[Co(en)_3]^{2+}$ species which is axially elongated due to Jahn–Teller distortion [53], followed by intramolecular back electron transfer in the cyano-bridged intermediate. It is not yet clear why the ion pairs of the corresponding Cr^{III} complexes behave completely differently.

The spin state, however, has not yet been unambiguously assigned to the Cr^{II} intermediates formed primarily upon IPCT photolysis of the latter ion pairs [46]. There is a striking variation over orders of magnitude of the quantum yields of Co^{II} formation from ion pairs $\{[Co(sep)]^{3+};RCOO^-\}$ in aqueous solution depending on R [48]. A factor of two or so for α-hydroxycarboxylates, when compared with simple carboxylates, could have been explained in terms of secondary redox reactions of strongly reducing [54] hydroxyalkyl and formyl radicals respectively, formed as the result of decarboxylation of the short-lived primary acyloxy radicals. The observed quantum yields, however, range between $\Phi_p = 0.44$ for oxalate and less than 10^{-3} for acetate as counter ions. Interestingly enough, it has been shown that the oxalate anion radical, $C_2O_4^{-\bullet}$, is not only an oxidizing species with $E^0 = 2.1$ V vs. the normal hydrogen electrode (NHE), but is also a strong reductant with $E^0 = -3.2$ V vs. NHE [55,56]. Hence, this radical should be able to undergo a second in-cage electron transfer reaction under concomitant formation of $[Co(sep)]^+$. The latter species, however, has not yet been detected.

Photoinduced electron transfer in ion pairs of coordination compounds is of particular interest with respect to spectral sensitization, since the long-wavelength absorption of one of the components, e.g. a dyestuff, can be exploited. If the excitation of the sensitizer is followed by fast electron transfer, the subsequent reactions of the successor pair $\{A^\bullet;D^\bullet\}$ can be described by the same kinetic model as depicted in Scheme 3. However, it is a peculiarity of photoinduced electron transfer that inter-system crossing (ISC) of the excited state sensitizer can occur prior to electron transfer, Scheme 4.



Scheme 4.

The excited state ion pair $\{{}^{**}A^+;D^-\}$ (the double asterisk denotes a different spin multiplicity compared with $^*A^+$) and the successor pair $\{A^\bullet;D^\bullet\}$ are no longer correlated with the ground state ion pair $\{A^+;D^-\}$ with respect to the spin state. Hence, subsequent reactions from the successor pair ($k_{p,cage}$, k_{ce}, $k_{p,bulk}$) can efficiently compete with the spin-forbidden back electron transfer (k_{back}).

Depending on the irradiation wavelength, both optical and photoinduced electron transfer from the anion have been shown to occur in the ion pair

{$[Co(NH_3)_6]^{3+}$;BPh_4^-} [57]. Since the fluorescence of BPh_4^- is quenched by $[Co(NH_3)_6]^{3+}$, the anion most likely reacts from its singlet excited state. Hence, the similar quantum yields upon 254 ($\Phi = 1.10$), 313 (1.37) and 365 nm (0.83) irradiation corresponding to the local excitation of BPh_4^- and IPCT excitation respectively, may be interpreted in terms of the formation of the same successor pair from both reaction pathways. A third pathway, i.e. the local excitation of $[Co(NH_3)_6]^{3+}$ followed by electron transfer from the ground state counter ion, was not discussed in that paper but is likely operative upon long-wavelength irradiation ($\Phi = 0.18$ at 436 nm).

A number of ion pairs {$[Co(en)_3]^{3+}$;D^-} show up photo-redox reactivity upon ligand-field excitation, i.e. beyond the IPCT absorption threshold [13,38,52]. The photo-redox reactivity of cobalt(III)amines upon ligand-field excitation has been tentatively attributed to rapid ISC from the primarily formed singlet to the quintet state of Co^{III} [52]. From the latter state the thermodynamically stable high-spin cobalt(II) complexes may be formed directly by one-electron reduction, whereas reduction from the singlet and triplet manifold, should lead to low-spin Co^{II}. Although the quintet state of Co^{III} is shorter lived than the ca. 10 ns assumed earlier [52,58], its lifetime of 500 ps [59] is long enough to undergo electron transfer reactions with the counter ion. The quantum yields upon 514 nm excitation of ion pairs {$[Co(en)_3]^{3+}$;D^-} decrease with increasing oxidation potential of the anion: $[Fe(CN)_6]^{4-}$ ($E^0 = 0.36$ V) $\Phi = 0.14$; $[Ru(CN)_6]^{4-}$ (0.86 V) $\Phi = 0.01$; I^- (1.33 V) $\Phi = 0.003$. Ion pairs with bromide (1.85 V) and oxalate (2.1 V) ions do not undergo any photo-redox reaction under the same experimental conditions [38].

Ligand-field excitation of ion pairs {$[Cr(en)_3]^{3+}$;$[M(CN)_6]^{4-}$} (M = Fe, Ru, Os) most likely does not induce electron transfer, but substitution of an amine ligand by the cyanometallate [33,46].

4. Conclusion

Ion pairs of coordination compounds, compared with the separate components, may exhibit a number of novel interesting spectroscopic and photochemical properties. Permanent photoproducts are obtained from both optical and photoinduced electron transfer reactions if back electron transfer is suppressed by rapid decomposition of the successor pair components. Cobalt(III) complexes [48–50], onium ions [51,60], carboxylates [48] and tetraarylborates [57] are promising components for light-sensitive ion pairs. Reactive species, like coordinatively unsaturated complexes, free radicals and metal ions in unusual oxidation steps, may be formed from ion pairs under mild conditions using visible light. Light-sensitive ion pairs of coordination compounds may find use as photoinitiators for microimaging and curing applications [57], as well as in organic synthesis. Selective formation of ketones and aldehydes from the corresponding alcohols in a photoinduced chain reaction, initiated by the IPCT excitation of diphenyliodonium cyanometallate ion pairs, has been observed very recently [47].

Acknowledgements

Support from the Alexander von Humboldt-Stiftung and helpful discussions with Professor H. Hennig, Professor R. van Eldik and Professor A. Vogler are kindly acknowledged.

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