

Photoluminescence Electron-Transfer Quenching of Rhenium(I) Complexes with Organic Sulfides

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Abstract Electron-transfer(ET) from organic sulfides to excited state rhenium(I)-based heteroleptic tricarbonyl complexes $[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$ (**I**) and $[\text{Re}(\text{bpy})(\text{CO})_3(\text{ind})]^+$ (**II**) in acetonitrile solution is facile and luminescence quenching constants, k_q , are in the range 10^5 – $10^8 \text{ M}^{-1}\text{s}^{-1}$. The detection of the sulfide radical cation in this system using time-resolved absorption spectroscopy is a direct evidence for the ET nature of the reaction. The k_q values for the quenching of Re(I)-complexes with organic sulfides are analyzed with a scheme involving rate controlling electron transfer process. The measured rate constants for the electron transfer (ET) reaction are close to the values calculated from Marcus theory.

Keywords Electron transfer · Rhenium(I) complex · Sulfur radical cation · Marcus theory

Introduction

Organic sulfides undergo electron transfer reaction in the presence of suitable electron acceptors (oxidants) because of their low ionization potentials [1], and the resultant sulfide radical cations have biological and medical implications [2–5]. Sulfur-centered radicals have recently gained prominence as possible intermediates in redox reactions of biomolecules and it is essential to characterize model

systems where physical and chemical properties can be determined [6]. Considerable attention has been devoted to the chemistry of sulfur-centered radicals and radical cations because of their importance as intermediates in many chemical processes including those of organic synthesis [7, 8], environmental [9, 10] and biological significance [11].

Many transition metal-polypyridine complexes display an intense and long-lived emission in the visible region and possess rich photoredox chemistry [12, 13]. Particularly the photophysical and photochemical properties of rhenium (I)—tricarbonyl, $\text{Re}^I(\text{CO})_3$, complexes coordinated to mono and bidentate ligands have attracted a great deal of attention for the past three decades [14–16]. The accessible excited states, metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT) and/or intraligand charge transfer (ILCT), are generally involved with the observed luminescence at room temperature [17]. The excited state properties of these complexes can be varied systematically by changing the structure of the mono as well as bidentate ligands. Hence the Re(I)-polypyridine complexes have been used as photosensitizers, efficient photocatalysts for CO_2 reduction [18], building blocks for luminescent supramolecules [19, 20], as sensors [21], for cell imaging [22], as probes for biological molecules [23] and surfactants [24].

Though Re(I)-complexes undergo interesting photoinduced electron transfer reactions with a variety of organic molecules [25–28], as far as we know, there is no report available on the photoredox reactions of these complexes with biologically important organic sulfides. Allen Gnanaraj et al. [29] reported the results on the excited state electron transfer reactions of chromium(III)-polypyridyl complexes with various organic sulfides and applied Marcus theory

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successfully to this reaction. Thanasekaran et al. [30] reported the emission quenching of $[\text{Ru}^{\text{II}}(\text{bpz})_3]^{2+}$ ($\text{bpz} = 2,2'$ - bipyrazine) ion with various organic sulfides. Ramamurthy et al. [31] studied the photoinduced electron transfer reaction of sulfides with pyrylium derivatives and Rajkumar et al. [32] reported the photoinduced electron transfer reaction of $[\text{Ru}(\text{dcbpy})_3]^{2+}$ ($\text{dcbpy} = 4,4'$ - dicarboxy-2,2'- bipyridine) ion with organic sulfides.

Since the Re(I) complexes are extremely photostable and possess useful excited state properties including long lifetime, high quantum yield, and high emission polarization in the absence of rotational diffusion [33] there is a rapid development of transition metal-ligand complexes as biophysical probes and/or chemical sensors [34]. Apart from the above advantages, Re(I) complexes display large Stokes shifts, which eliminates the problems of self-quenching. Herein we report our results on the excited-state electron transfer reactions of heteroleptic Re(I)-complexes with a series of organic sulfides. The formation of sulfide cation radical as the intermediate is observed for the first time using the Re(I)-complexes as photosensitizer. The efficiency of the quenching rate reveals that the one electron oxidation of organic sulfides resulting in the formation of radical intermediate is facile. Thus this method can be used conveniently for the generation of sulfur centered radicals which are of biological and pharmaceutical importance. In the present study $[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$ (**I**) and $[\text{Re}(\text{bpy})(\text{CO})_3(\text{ind})]^+$ (**II**) are synthesized, complex **II** for the first time, and the excited state ET reaction of these Re(I) complexes (Chart 1 shows structure of complexes **I** and **II**) with organic sulfides studied by luminescence quenching as well as transient absorption techniques.

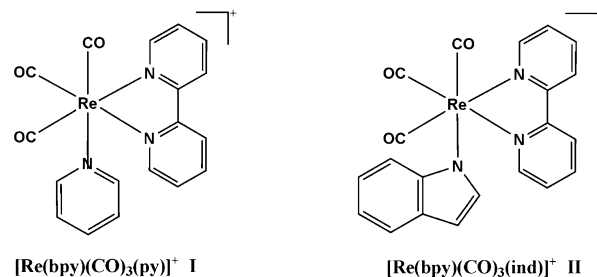
Experimental

Materials

The chemicals used in this study $\text{Re}_2(\text{CO})_{10}$, 2,2'-bipyridine, pyridine (py) and indole (ind) were obtained from Aldrich. $\text{Re}(\text{CO})_5\text{Br}$ was obtained by oxidative addition of Br_2 to $\text{Re}_2\text{CO}_{10}$ [35]. The complexes **I** and **II** were synthesized using reported method [36].

The complex $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$ was prepared from $[\text{Re}(\text{CO})_5\text{Br}]$ by the general procedure described by Meyer et al. [37]. A Sample of 0.1 g (0.197 mmol) $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$ and 0.0557 g (0.214 mmol) AgCF_3SO_3 were refluxed in 25 ml THF for 3 h under nitrogen atmosphere. After AgBr filtration, 0.023 g (0.197 mmol) of indole was added and refluxed for overnight in inert atmosphere. Then the mixture was evaporated to dryness. The resultant residue was dissolved in small amount of acetone and the saturated solution of NH_4PF_6 was added. The pure $[\text{Re}(\text{CO})_3(\text{bpy})$

Structure of Re(I) complex



Structure of Quenchers

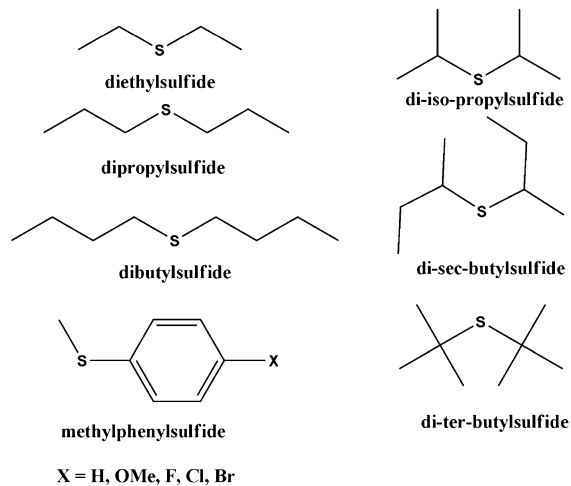


Chart 1 Structure of Re(I) complexes and the quenchers used in the present study

(ind)] PF_6 was precipitated and dried. Yield = 56%. $\nu_{\text{max}}/\text{cm}^{-1}$ 2036, 1920.. ESI-MS m/z : 542.07 for $[\text{Re}(\text{bpy})(\text{CO})_3(\text{ind})]^+$, 426.98 for $[\text{Re}(\text{bpy})(\text{CO})_3]^+$

Absorption and Emission Spectral Measurements

The absorption spectral measurements were carried out using Analtikajena Specord S100 Diode array spectrometer. Emission intensity measurements were carried out using JASCO FP—6300 spectrofluorometer. All the sample solutions used for emission measurements were deaerated for about 30 min by dry nitrogen gas purging by keeping solutions in cold water to ensure that there is no change in volume of the solution.

Luminescence Lifetime Measurements

The excited-state lifetimes of complexes **I** and **II** (1×10^{-4} M) in acetonitrile (AN) solution at 298 K were measured using time—correlated single photon counting (TCSPC) technique and the details of measurements are given in our previous report [38].

Electrochemical Measurements

The redox potential of **II** was determined by cyclic voltammetric technique using EG&G Instruments Princeton Applied Research Potentiostat Galvanostat model 283. Samples of 1 mM solutions of complex **II** for the electrochemical studies were prepared in acetonitrile, Tetrabutyl ammonium hexafluorophosphate (TBAH) was used as the supporting electrolyte. A Pt electrode (working electrode) and a standard Ag/AgCl reference electrode were used in the electrochemical measurements. Cyclic voltammograms were recorded after purging the solution with dry nitrogen gas for 30 min.

Luminescence Quenching Measurements

Sample solutions of the metal complex and the quencher were freshly prepared for each measurement. The sample solutions were purged carefully with dry nitrogen for 30 min. The luminescence measurements were performed at different quencher concentrations and the quenching rate constant, k_q , values were determined from the Stern–Volmer plot using the equations given below.

$$I_0/I = 1 + K_{sv}[Q] \quad (1)$$

$$K_{sv} = k_q\tau^0 \quad (2)$$

Here I_0 and I are the luminescence intensities of Re(I) complex in the absence and presence of quencher respectively, K_{sv} , the Stern–Volmer constant, k_q , the quenching rate constant and τ^0 , the luminescence lifetime of Re(I) in the absence of quencher.

Transient Absorption Spectral Measurement

Transient absorption measurements were made with laser flash photolysis technique using an applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser as the excitation source. The time dependence of the luminescence decay is observed using a Czerny-Tuener monochromator with a stepper motor control and a Hamamatsu R-923 photomultiplier tube. The production of the excited state on exposure to 355 nm was measured by monitoring (pulsed Xenon lamp of 250 W) the absorbance change. The change in the absorbance of the sample on laser irradiation was

used to calculate the rate constant as well as the time-resolved absorption transient spectrum. The change in the absorbance on flash photolysis was calculated using the expression

$$\Delta A = \log(I_0/(I_0 - \Delta I)) \quad (3)$$

$$\Delta I = (I - I_t) \quad (4)$$

where ΔA is the change in the absorbance at time t , I_0 is the voltage after flash, I is the pretrigger voltage and I_t is the voltage at particular time. A plot of $\ln(\Delta A_t - \Delta A_\infty)$ vs time gives a straight line. The slope of the straight line gave the rate constant for the decay. The reciprocal of these values gave the lifetime of the triplet. The time-resolved transient absorption spectrum was recorded by plotting the change in absorbance at a particular time vs wavelength.

Results and Discussion

Synthesis and Characterization

The structures of Re(I) complexes and the quenchers used in the present study are shown in Chart 1. Rhenium(I) complexes have been prepared by an easy, well defined two step synthetic procedure. The reaction of starting material, $\text{Re}(\text{CO})_5\text{Br}$, with the bidentate ligand containing sp^2 nitrogen donors belonging to an extended π -system (2, 2'-bipyridine, bpy) leads to the formation of *fac*-[Re(bpy)(CO)₃Br] species which is moisture stable and kinetically inert, this latter feature being typical of the low spin d^6 Re^I cation. The Br[−] can be removed in a second separate step (reflux with $\text{Ag}(\text{CF}_3\text{SO}_3)$) and substituted with pyridine (py)/indole (ind), to get *fac*-[Re(bpy)(CO)₃(py)]⁺ (**I**) and [Re(bpy)(CO)₃(ind)]⁺ (**II**) respectively which are also air and moisture stable and kinetically inert.

Table 1 summarizes the IR carbonyl stretching frequencies, electronic absorption and emission spectral data and excited state lifetime of precursor, [Re(CO)₃(bpy)Br], and complexes **I** and **II**. The ground state IR spectrum of precursor shows three CO stretching frequencies A'(1) (axial band), A'(2) and A'' (equatorial band) respectively. In both complexes the A'(1) vibrational frequency value is higher than A'(2) and A'' vibrational modes. In complexes **I** and **II** upon introduction of spectator ligands py and ind,

Table 1 Photophysical and photochemical properties of complexes **I** and **II** in AN at 298 K

Complex	λ_{abs} , nm	λ_{em} (nm)	τ (ns)	ν_{CO} , cm^{-1}	$E_{1/2}^{\text{ox}}/\text{V}$	$E_{1/2}^{\text{red}}/\text{V}$
[Re(CO) ₃ (bpy)Br]	372	605	51	2023, 1917, 1900	–	–
I ^a	366	558	241	2038, 1928	+1.74	−1.39
II	346	551	230	2036, 1920	+1.45	−1.55

^a ref. [36]

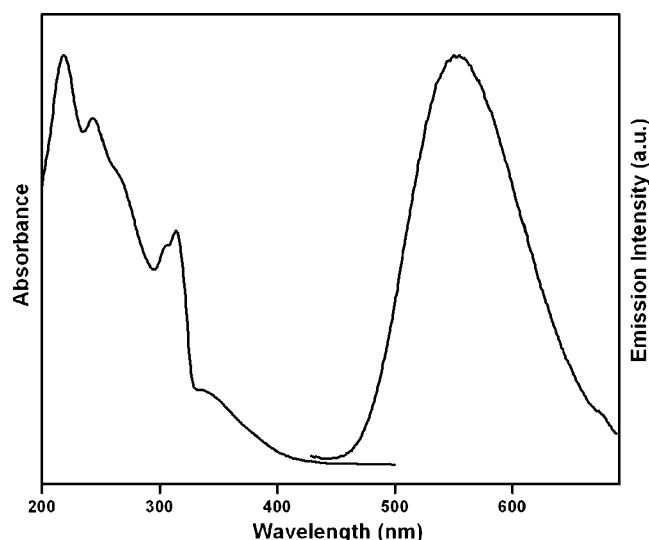


Fig. 1 Normalized absorption and emission spectra of complex **II** in AN at 298 K

increment of the stretching frequencies is observed. This increase in $\nu(\text{CO})$ stretching frequency denotes decrease of π —back bonding towards the carbonyl ligands, due to the decreased electron density on the Re(I) center because of the coordination of π —accepting ligands. The energy gap between $A'(2)$ and A'' vibrational modes are small, hence they are merged into a single frequency [39]. The energies of the $\nu(\text{CO})$ stretching frequencies of complex **II** shifted to the lower energy with respect to complex **I** due to the electron donating property of indole ligand [37].

The absorption and emission spectra of **II** in acetonitrile are shown in Fig. 1. The electronic absorption spectrum of

complex **II** reveals strong absorption bands at 210–315 nm and less intense absorption shoulders at 346 nm. With reference to previous studies on related Re(I) complexes [40–43], these strong high energy absorption bands are assigned to the ligand centered (LC) π – π^* transition and low energy absorption shoulders to spin allowed metal to ligand charge transfer $^1\text{MLCT}$ transition from the Re $d\pi$ -orbital to the π^* orbital of the ligand ($d\pi(\text{Re}) \rightarrow \pi^*$ (diimine)). The $^3\text{MLCT}$ emission of complex **II** is observed at 551 nm in acetonitrile at RT. Because of the electron donating property of indole ligand, the absorption and emission maxima of complex **II** gets blue shifted from the complex **I** [37]. Lifetime of complex **II** is also close to the related Re(I) complex **I**. The absorption ($\lambda_{\text{abn.}}=362$ nm) and emission ($\lambda_{\text{emn.}}=560$ nm) maxima of complex **I** are found to be close to the literature ($\lambda_{\text{abn.}}=366$ nm; $\lambda_{\text{emn.}}=558$ nm) values [36].

Spectral Studies

In order to check the ground state complex formation between the photosensitizer (Re(I) complexes) and quencher (sulfides) we have recorded the absorption spectra of Re(I) complexes in the presence of different [quencher]. There is no appreciable change in the absorption spectra of Re(I) complexes when the concentration of the quencher is increased. From this observation we can conclude that there is no ground state complex formation between Re(I) complexes and sulfide and the contribution from the static quenching is negligible, and thus the dynamic quenching is the predominant process in this system. This is further confirmed by luminescence quenching study (vide infra).

Table 2 Bimolecular quenching rate constants, (k_q), for complexes **I** and **II** by organic sulfides in AN at 298 K

Quencher (E^0_{ox} (V) ^a)	Complex I					Complex II				
	ΔG^0 , eV	$k_q(\text{exp.})$, $\text{M}^{-1}\text{s}^{-1}$	$k_q(\text{cal.})$, $\text{M}^{-1}\text{s}^{-1}$	$k_{23}(\text{exp.})$, $\text{M}^{-1}\text{s}^{-1}$	$k_{23}(\text{cal.})$, $\text{M}^{-1}\text{s}^{-1}$	ΔG^0 , eV	$k_q(\text{exp.})$, $\text{M}^{-1}\text{s}^{-1}$	$k_q(\text{cal.})$, $\text{M}^{-1}\text{s}^{-1}$	$k_{23}(\text{exp.})$, $\text{M}^{-1}\text{s}^{-1}$	$k_{23}(\text{cal.})$, $\text{M}^{-1}\text{s}^{-1}$
Methyl phenyl sulfide (1.53)	0.54	9.1×10^7	8.8×10^6	6.4×10^7	6.2×10^6	0.58	9.2×10^7	8.1×10^6	7.1×10^7	5.9×10^6
Methyl <i>p</i> -methoxyphenyl sulfide (1.26)	0.27	1.5×10^8	9.3×10^7	9.0×10^7	5.0×10^7	0.31	2.1×10^8	9.3×10^7	1.1×10^8	5.0×10^7
Methyl <i>p</i> -fluorophenyl sulfide (1.54)	0.55	5.9×10^6	7.7×10^5	3.9×10^6	5.2×10^5	0.59	6.4×10^6	8.2×10^5	5.2×10^6	5.6×10^5
Methyl <i>p</i> -chlorophenyl sulfide (1.55)	0.56	5.4×10^6	6.5×10^5	3.3×10^6	4.2×10^5	–	–	–	–	–
Methyl <i>p</i> -bromophenyl sulfide (1.56)	0.57	5.1×10^6	7.8×10^5	3.1×10^6	4.8×10^5	–	–	–	–	–
Diethyl sulfide (1.65)	0.66	2.1×10^6	9.2×10^5	1.5×10^6	6.6×10^5	0.70	5.3×10^6	7.4×10^5	4.0×10^6	5.6×10^5
Dipropyl sulfide (1.63)	0.64	2.6×10^6	8.2×10^5	1.2×10^6	3.8×10^5	–	–	–	–	–
Diisopropyl sulfide (1.63)	0.64	2.0×10^5	7.4×10^5	1.5×10^5	5.9×10^5	–	–	–	–	–
Dibutyl sulfide (1.63)	0.66	3.8×10^6	8.4×10^5	1.4×10^6	3.1×10^5	0.68	4.4×10^6	9.1×10^5	1.6×10^6	3.7×10^5
Di- <i>sec</i> -butyl sulfide (1.65)	0.66	1.9×10^5	7.9×10^5	1.1×10^5	4.8×10^5	–	–	–	–	–
Di- <i>tert</i> -butyl sulfide (1.65)	0.66	3.4×10^5	7.2×10^5	2.9×10^5	5.2×10^5	–	–	–	–	–

^a ref [32, 49]

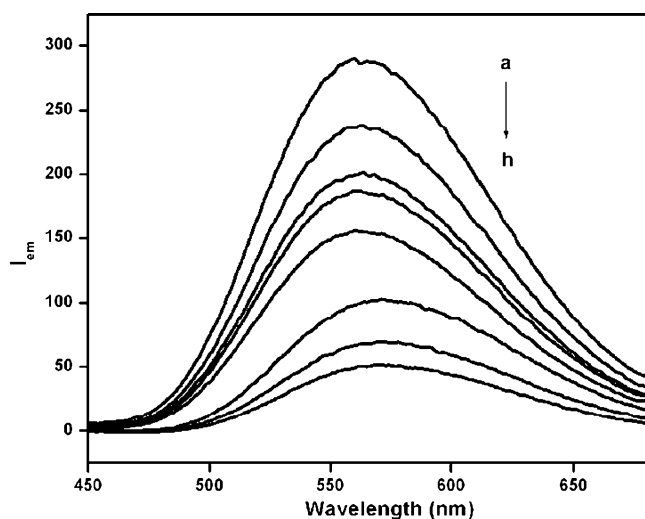


Fig. 2 Luminescence intensity quenching of complex **I** (1×10^{-4} M) with MPS in the concentration (a) 0 (b) 0.02 M (c) 0.04 M (d) 0.06 M (e) 0.1 M (f) 0.2 M (g) 0.3 M (h) 0.4 M in AN. Ex. Max. 360 nm

Luminescence Quenching Rate Constants

The bimolecular quenching rate constant, k_q , values for the luminescence quenching of **I** and **II** with organic sulfides (aryl methyl and dialkyl sulfides) were measured using Eqs. 1 and 2 and the k_q values are collected in Table 2. Linear Stern–Volmer plots of I_0/I vs. $[Q]$ were observed for all quenchers indicating that the luminescence quenching process is dynamic [27, 44–46]. Figure 2 shows luminescence intensity quenching of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$ complex at various concentration of methyl phenyl sulfide and the corresponding Stern–Volmer plot is shown in Fig. 3. The k_q values for the luminescence quenching of complexes **I** and **II** with different sulfides are in the order of 10^5 –

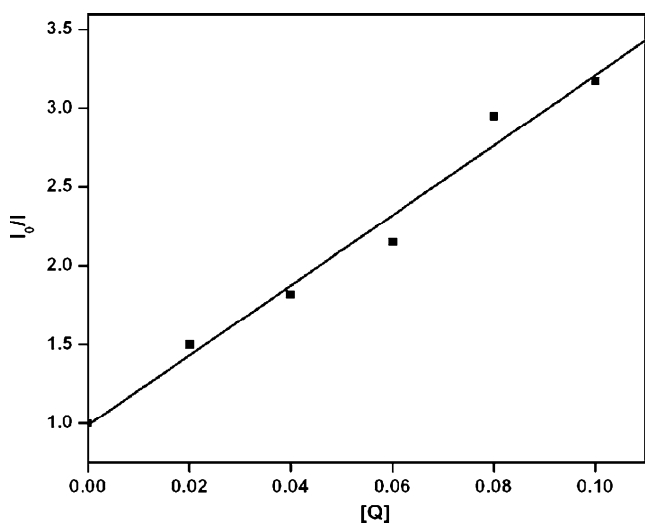
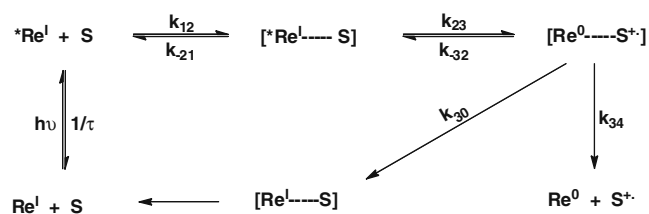


Fig. 3 Stern–Volmer plot for the reductive quenching of complex **I** with different $[\text{MPS}]$ in AN



Scheme 1 Mechanism for the luminescence quenching of Re(I)-polypyridyl complexes with organic sulfides

$10^8 \text{ M}^{-1}\text{s}^{-1}$. The observed k_q value for the quenching of complex **I** with methyl phenyl sulfide (MPS) is found to be $9.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ and for complex **II** the k_q value is $9.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. When we introduce the electron donating group like methoxy at *para*-position of the thioether moiety, there is an increase in the quenching rate and the electron withdrawing groups like F, Cl, and Br decrease the quenching rate [32]. From this observation we conclude that the interaction between Re(I) complexes and the quencher is sensitive to the structure of the quencher. For the excited state reactions of transition metal complexes, either the energy or electron transfer quenching process has been considered [47]. Here the possibility of energy transfer process is negligible because, the triplet energy level of sulfide is $>3.0 \text{ eV}$ [48–50] which is above the available excitation energy of Re(I) complexes ($\sim 2.3 \text{ eV}$). So we can postulate that the reaction of sulfide with the luminescent Re(I)-complexes must be a dynamic quenching process via an electron transfer mechanism (Scheme 1) which is further confirmed from the transient absorption spectral study and by correlating the quenching rate constant (k_q) data with the oxidation potential of sulfides. The plot between $\log k_q$ and oxidation potential of sulfides is linear (Fig. 4), which acts as an additional support for an electron transfer process.

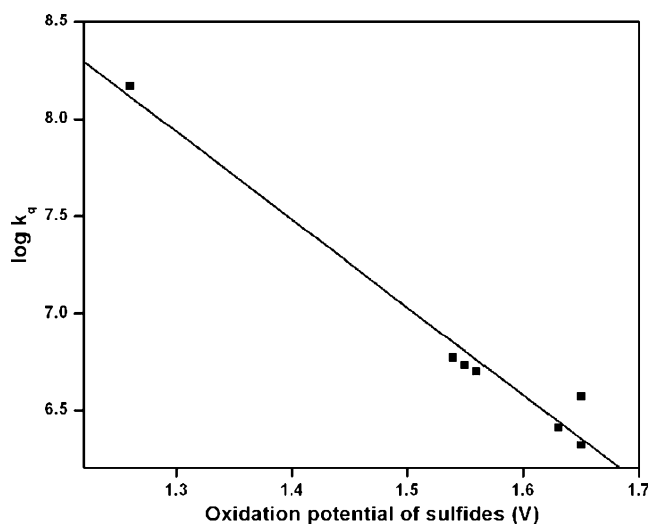


Fig. 4 Plot of $\log k_q$ vs the oxidation potential of sulfides

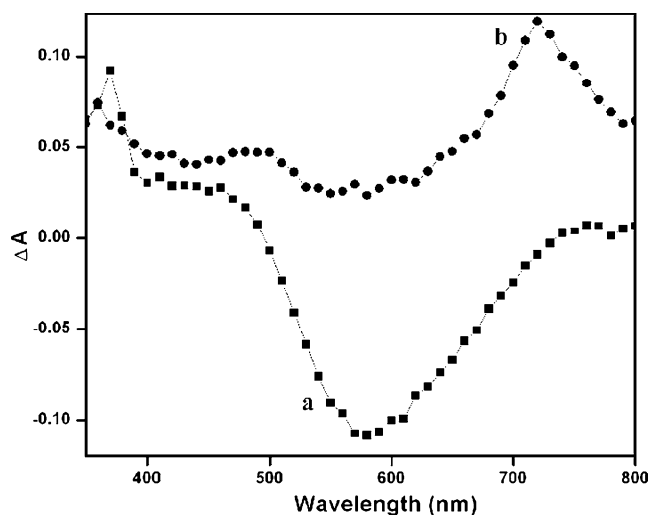


Fig. 5 Transient absorption spectra obtained by laser flash photolysis of (a) complex **I** (■) and (b) complex **I** in the presence of MPS (●) in AN, recorded following 355 nm laser pulse excitation

Transient Absorption Spectral Studies

To gain more insight into nature of the quenching mechanism, analysis of the transient species is also made for Re(I)-complexes in the absence as well as in the presence of quenchers (sulfides). Monochromatic flash irradiation of complexes **I** and **II** in acetonitrile was used to perform the transient absorption spectral measurements. The transient absorption spectra recorded following the irradiation of complex **I** (1×10^{-4} M) in the presence of MPS (0.01 M) in AN by 355 nm excitation is shown in Fig. 5. The absorption at 370 nm corresponds to bipyridine

anion radical and the strong bleaching of MLCT emission occurs at 570 nm. The new absorption peaks at 490–550 nm and 720 nm were observed in the presence of MPS. In accordance with the well-known absorption spectrum of the methyl phenyl sulfide cation radical reported by Baciocchi et al. [51], Yokoi et al. [52], Rajagopal et al. [32, 53] and others [54–56] the absorption band maximum at 490–550 nm corresponds to the sulfide cation radical and the band around 720 nm may be due the dimer of MPS radical cation [31]. The small band at 420 nm in the presence of MPS is assigned for formation of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^0$ species. The transient absorption spectrum recorded following the irradiation of complex **II** (1×10^{-4} M) in the absence and in the presence of DES (0.01 M) at 355 nm in AN is shown in Fig. 6. This transient spectrum also shows bipyridine anion absorption at 370 nm, strong bleaching of MLCT emission at 570 nm (Fig. 6a). There is no absorption at 510 nm in the absence of DES (Fig. 6a), but in the presence of DES a new absorption band at 510 nm was observed (Fig. 6b) which is assigned for the formation of diethyl sulfide radical cation. The decay kinetics of complex **II** measured at 510 nm in the absence and presence of DES are shown in Fig. 7. The formation of a sulfide cation radical is observed for the first time in the $^3\text{MLCT}$ excited state electron transfer reaction of Re(I)- complex with MPS and DES. Thus it is clear that, in the presence of MPS and DES, the triplet state of Re(I) in AN is efficiently quenched by the transfer of an electron from sulfide, to form the reduced species of the Re(I) and a radical cation of sulfide.

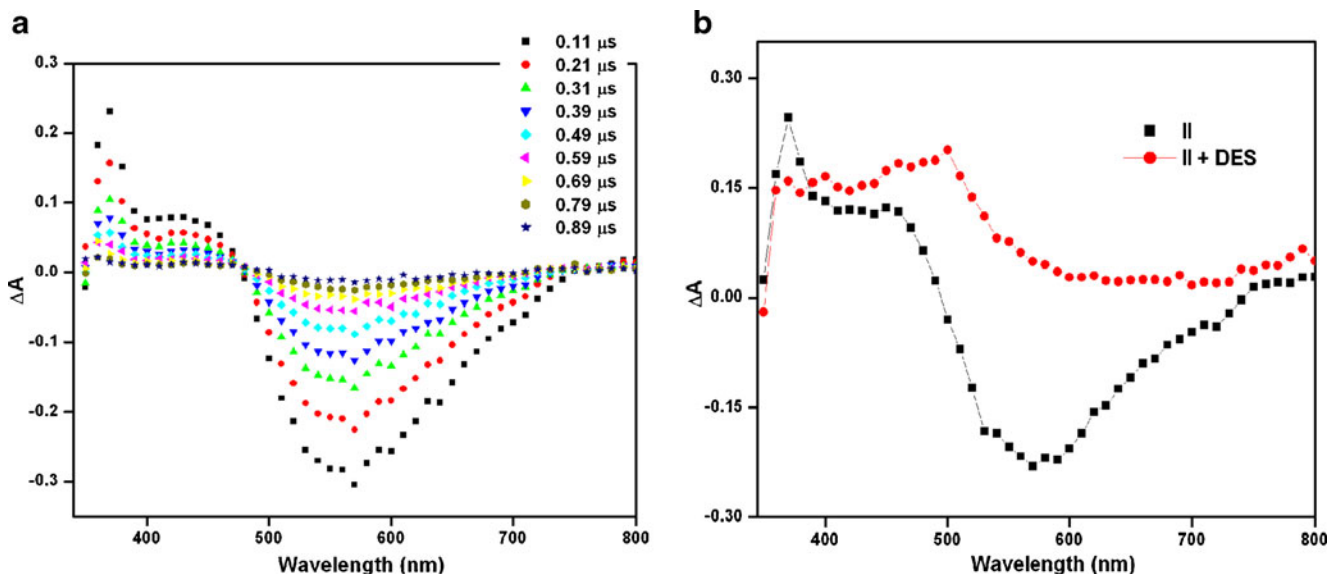


Fig. 6 Transient absorption spectra obtained by laser flash photolysis of (a) complex **II** and (b) complex **II** in the presence of DES in AN, recorded following 355 nm laser pulse excitation

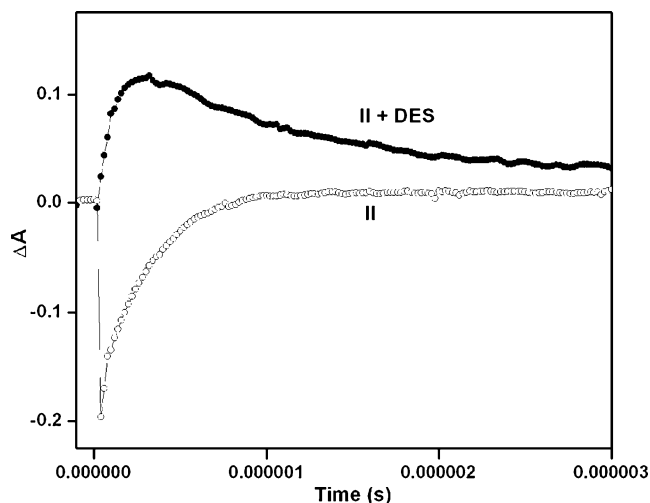


Fig. 7 Transient kinetics of complex **II** was measured at 510 nm in the absence (○) and presence (●) of DES in AN

It is interesting to look at the nature of the products if the reaction is carried out in aqueous medium. If

water is used as the reaction medium, the sulfide cation radical ($S^{+\bullet}$) formed due to ET from sulfide to the excited state $Re(I)$ complex (Scheme 1) will interact with water to form finally the sulfoxide as the product. The steps that may be involved in the formation of sulfoxide may be represented as steps shown in Scheme 2. It is pertinent to point out that we have presented the detailed mechanism for the formation of aromatic sulfoxide from the corresponding sulfide by using $Ru(III)$ —polypyridyl complexes generated photochemically from $Ru(II)$ complexes as oxidant [48].

Application of Theory of Electron Transfer

After establishing electron transfer nature of the reaction, we have applied the semiclassical theory of ET (Eq. 5 [57–60]) to calculate the rate constant for the electron transfer reaction of the excited state $Re(I)$ complex with organic sulfides.

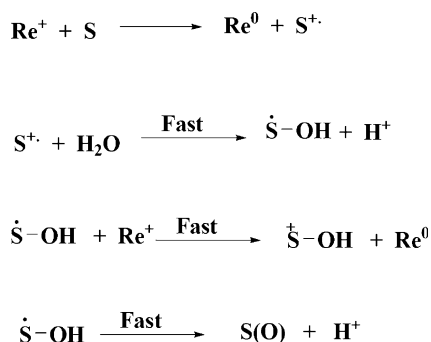
$$k_{et} = (4\pi^2/h)|H_{DA}|^2(4\pi\lambda kT)^{-1/2} \sum_{m=0}^{\infty} (e^{-s} S^m/m!) \exp[-(\lambda + \Delta G^0 + mh\nu)^2/4\lambda kT] \quad (5)$$

Here H_{DA} is the electronic coupling coefficient between the redox centers, ΔG^0 is the free energy change, the reorganization energy λ is composed of solvational λ_o and vibrational λ_i contributions with $s=\lambda_i/h\nu$, ν is the high-energy vibrational frequency associated with the acceptor, and m is the density of product vibrational levels. The terms h and k are Planck and Boltzmann constants respectively. The value of λ_o can be evaluated classically by using the dielectric continuum model (Eq. 6)

$$\lambda_o = e^2/4\pi\epsilon_0(1/2r_D + 1/2r_A - 1/d)(1/D_{op} - 1/D_s) \quad (6)$$

where, e is the transferred electronic charge, ϵ_o is the permittivity of free space and D_{op} and D_s are the optical and static dielectric constants respectively. The terms r_D and

r_A are the radii of the electron donor and acceptor respectively, and $d (= r_D + r_A)$ is the separation distance between the donor and acceptor in the encounter complex. The values of r_D and r_A are estimated by the MM2 molecular model. The value of λ_o estimated from Eq. 6 falls in the range 0.77–1.05 eV for this redox system.



Scheme 2 Steps involved in the formation of sulfoxide in the presence of water

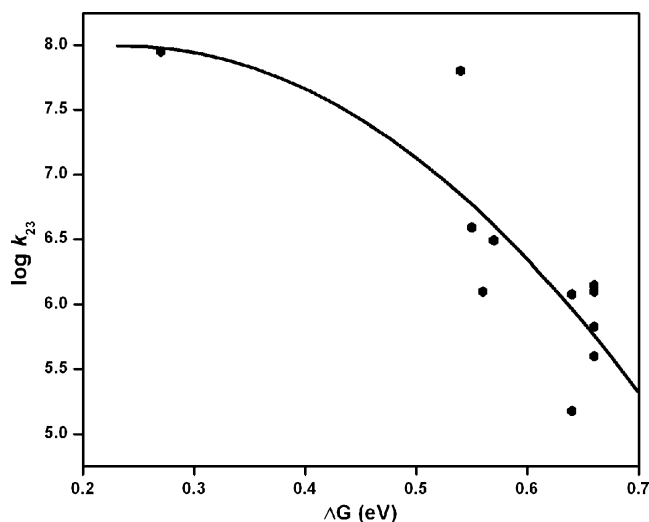


Fig. 8 Plot of $\log k_{23}$ vs ΔG^0 (eV) for complex **I**. (The points represent the experimental data, and the solid curve is the best fit of the experimental rate constant data using semiclassical theory of electron transfer)

According to Rehm and Weller, the free energy change of electron transfer can be calculated from Eq. 7 [61]

$$\Delta G^0 = E(D/D^+) - E(A/A^-) - E_{0-0} - e^2/a\epsilon \quad (7)$$

where $E(D/D^+)$ is the oxidation potential of donors (organic sulfides), $E(A/A^-)$ the reduction potential of Re(I) complex and $e^2/a\epsilon$ a columbic term. The ΔG^0 values thus estimated for the redox complex, *Re(I)-organic sulfide, in acetonitrile are listed in Table 2.

Since it is established that the quenching occurs via ET, the redox quenching process, as shown in Scheme 1, can be discussed. According to Scheme 1, the excited state acceptor (*Re^I) and the ground-state donor (sulfides S) diffuse together to form an encounter complex (*Re^I...S). This encounter complex then undergoes a reorganization to reach the transition state where ET takes place from the donor to the acceptor to give an ion-pair species (Re⁰...S⁺). The parameters k_{12} and k_{21} are the diffusion-controlled rate constants for the formation and dissociation of the encounter complex, *Re^I...S, respectively. k_{23} and k_{32} are the forward and reverse ET rate constants respectively, and k_{34} is the sum of all the rate constants causing the disappearance of the ion-pair state (Re⁰...S⁺)

By applying steady-state approximation to the short-lived species in Scheme 1, Eq. 8 can be derived for the observed bimolecular quenching rate constant, k_{obs} (k_q).

$$k_{\text{obs}}(k_q) = k_{12}/(1 + (k_{12}/k_{23}K_{\text{eq}})) \quad (8)$$

K_{eq} is the equilibrium constant for the formation of the encounter complex and k_{12} is the rate constant for the diffusion process to form the encounter complex. The value of k_{12} is calculated from Eq. 9 [62].

$$k_{12} = 2RT/3000\eta[2 + r_D/r_A + r_A/r_D]f \quad (9)$$

where $f^{-1} = d \int e^{u/kT} dr/r^2$ with $U = Z_D Z_A e^2/D_s [e^{kd}/1 + Kd]e^{-kr}/r$ and $K = (8\pi e^2 N \eta / 1000 D_s kT)^{1/2}$, and η is the viscosity of the medium.

The diffusion rate constant, k_{12} calculated according to Smoluchowski equation for non-charged molecules, has a value of $2.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. K_{eq} was estimated using the Fuoss and Eigen Eq. 10 [63]

$$K_{\text{eq}} = (4\pi N d^3 / 3000) \exp(-w^r/RT) \quad (10)$$

where w^r is the work required to bring the reactants at the separation distance d . Since we use neutral quenchers throughout this study, w^r is zero. The K_{eq} value is found to be in the range of 1.1–2.7 M^{-1} for the reductive quenching of complexes **I** and **II**. Since the values of k_{12} and K_{eq} are known, the value of k_{23} , the rate constant for the process of ET in the encounter complex, can be calculated using Eq. 8.

The calculated rate constants for ET from sulfides to *Re(I) by applying semiclassical expression of ET along with experimentally observed values for the above ET reaction are given in Table 2. The k_q data in Table 2 show that the values calculated from semiclassical theory are in fair agreement with experimental values (Fig. 8) supporting our postulation of Scheme 1 as the mechanism of the reaction of excited state Re(I) complex with organic sulfides. The rate of electron transfer (k_{23} (k_{et})) increases by decreasing the free energy of the reaction. The calculated k_{et} values were also plotted against $-\Delta G^0$ values (Fig. 8). The data given in Fig. 8 show a close agreement between the experimental and calculated values.

Conclusion

The results observed in the present study establish that the ³MLCT excited state of heteroleptic Re(I) complex is efficiently quenched by organic sulfides in acetonitrile solution at room temperature. The transient absorption spectra and luminescence quenching data clearly show that the excited state of Re(I) complex undergoes rapid ET reactions with organic sulfides. The formation of sulfide cation radical was observed for the first time in the ³MLCT excited state electron transfer reaction of a Re(I) complex. In addition, the semiclassical theory of ET was successfully applied for the photoluminescence quenching of Re(I) complex with sulfides.

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