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Cage escape yields for photoinduced bimolecular electron transfer reactions of Re(I) complexes

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Abstract

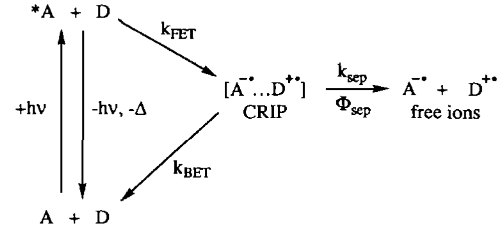
The quantum efficiencies for formation of free radical ions (Φ_{sep}) following electron transfer quenching of the metal-to-ligand charge transfer (MLCT) excited state of a series of $[(\text{diimine})\text{Re}^{I}(\text{CO})_3\text{L}]^+$ complexes by diaza[2.2.2]octane (DABCO) have been determined. The observed correlation between Φ_{sep} and the driving force for back electron transfer in the contact radical pair (ΔG_{BET}) is consistent with a Marcus inverted region dependence of the rate of back electron transfer on ΔG_{BET}. Comparison of the data for the present study with that for related systems suggests that: (i) the contact radical ion pair formed by electron transfer quenching has triplet spin multiplicity; (ii) the observed rate of charge recombination in the contact radical ion pair is controlled by the rate of triplet–singlet intersystem crossing.

Keywords: Photochemistry; Bimolecular electron transfer; Rhenium complexes; Carbonyl complexes; Bidentate amine complexes; Chelate complexes

1. Introduction

A wealth of information concerning factors that control electron transfer (ET) reactions has been obtained through the study of photoinduced ET [1]. Early studies examined bimolecular quenching of excited states and elucidated the dependence of the ET rate on the free energy change (ΔG_{ET}) [2–4]. However, owing to the kinetic limitations imposed by the rate of diffusion, the rates of highly exothermic Marcus inverted region ET reactions could not be determined by approaches that involve bimolecular quenching. More recently attention has turned to examining the rates of photoinduced forward and back electron transfer (FET and BET, respectively) in covalently linked donor–acceptor (D–A) molecules [5–21]. The covalently linked systems allow the use of ultrafast techniques to determine the kinetics of both FET and BET [22]. Studies of covalently linked systems led to the first experimental observation of the Marcus inverted region for highly exothermic ET reactions [23,24].

Concurrent to the studies of ET in covalently linked D–A systems, several groups examined the quantum efficiency for formation of free radical ions (Φ_{sep}, Scheme 1) following photoinduced bimolecular ET [25–36]. This work has been pursued with the understanding that Φ_{sep} depends on the rate of BET in the geminate contact radical ion pair (CRIP). Because BET within the CRIP is anticipated to be a first-order rate process, evaluation of Φ_{sep} provides an avenue to quantitatively determine k_{BET}/k_{sep}, where k_{BET} and k_{sep} are the first-order rates of BET within and escape from the CRIP, respectively. Farid and Gould and co-workers have successfully determined Φ_{sep} as a function of ΔG_{BET} for a broad series of CRIPs formed by photoinduced FET between aromatic organic D–A pairs [25–32]. Their work provides clear examples of Marcus inverted region behavior as well as significant insight concerning the dependence of k_{BET} on ΔG_{BET}, the structure of the CRIP, and solvent. Hoffman, Ohno and co-workers determined Φ_{sep} for CRIPs formed by photoinduced ET between a series of Ru(II)–polypyridyl complexes



Scheme 1.

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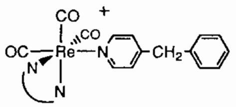
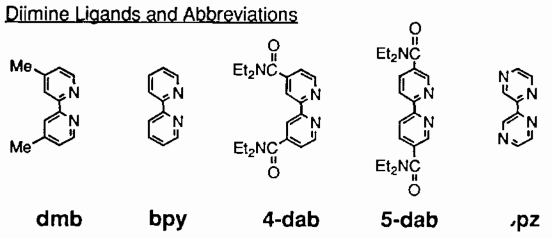
and *N*,*N*′-dimethyl-4,4′-bipyridinium (PQ^{2+}) [33–35]. This work has confirmed the Marcus inverted region for BET within CRIPs formed via encounter of the photoexcited Ru(II) complexes and PQ^{2+}.

Our group has carried out studies of the driving force dependence of intramolecular electron and energy transfer in several series of covalently linked D–A assemblies in which the chromophore/electron acceptor is based on the $(b)Re^{I}(CO)_3(py)^+$ unit (b = a bidentate diimine ligand and py is a monodentate pyridyl ligand) [19–21]. The $(b)Re^{I}(CO)_3(py)^+$ chromophore has proven to be well-suited for these studies because the first (diimine ligand-based) reduction potential and the energy of the $d\pi\ (Re) \rightarrow \pi^*$ diimine metal-to-ligand charge transfer (MLCT) excited state are readily tuned by variation of the substituents on the diimine ligand [37,38].

Recently we extended our studies of ET in $(b)Re^{I}(CO)_3(py)^+$ systems to examine the dependence of Φ_{sep} on ΔG_{BET} for CRIPs formed by bimolecular ET between the series of complexes (b)ReBP and 1,4-diazabicyclo[2.2.2]octane (DABCO). In the (b)ReBP series variation of the diimine ligand induces a substantial variation in the first reduction potential of the complexes [37]. As a result, examination of Φ_{sep} for photoinduced ET between the (b)ReBP series and DABCO allows elucidation of the dependence of the ratio k_{BET}/k_{sep} on ΔG_{BET} within CRIPs formed by ET quenching. Furthermore, since structural variations among the series of (b)ReBP complexes are comparatively small, k_{sep} is anticipated to be constant across the series and therefore the experimental Φ_{sep} values reflect the relative dependence of k_{BET} on ΔG_{BET} in the CRIPs.



(b)ReBP



The present communication reports the study of Φ_{sep} for CRIPs formed when DABCO quenches the photoexcited (b)ReBP complexes by ET. Values of Φ_{sep} were determined by using a laser flash photolysis technique that relies on an electron acceptor ‘probe’ to monitor the yield of free ions. The results indicate that k_{BET} within the organometallic CRIPs decreases as ΔG_{BET} becomes more exothermic in a manner that is qualitatively consistent with the predictions of Marcus theory. Interestingly, the correlation between k_{BET} and ΔG_{BET} for the (b)ReBP/DABCO CRIPs is remarkably similar to the dependence of k_{BET} on ΔG_{BET} observed for several series of covalently linked systems of the type, $(b)Re^{I}(CO)_3(py\text{-}D)^+$, where D is an organic electron donor [13,14,21]. The significance of the correspondence in the free energy dependence for the bimolecular and unimolecular ET systems will be discussed.

2. Experimental

2.1. General synthesis

All solvents and chemicals were of reagent grade and used without purification unless otherwise noted. The preparation and spectroscopic characterization of the (b)ReBP complexes has been described in previous publications [21].

2.2. Emission lifetime experiments

Emission lifetimes were determined by using time-correlated single photon counting (Photochemical Research Associates, FLI). Lifetimes were calculated by analysis of the experimental decays with the program DECAN, which allows for deconvolution of the instrument response function [39]. Stern–Volmer quenching experiments were carried out by measuring the emission lifetimes of degassed solutions of the metal complexes in CH_3CN solution for at least five different DABCO concentrations. In every case the Stern–Volmer plots of τ°/τ versus [DABCO] were linear.

2.3. Electrochemistry

Cyclic voltammetry was carried out on a Bioanalytical Systems CV-27 voltammograph. Experiments were conducted in a one-compartment cell with Pt disk working, Pt wire auxiliary and saturated sodium chloride calomel (SSCE) reference electrodes. Tetrabutylammonium hexafluorophosphate (TBAH) was used as the supporting electrolyte. The observed potentials were calibrated by using a ferrocene (Fc) internal standard and then converted to SCE by using the literature value for $E_{1/2}(Fc/Fc^+)$ (0.425 V versus SCE in CH_3CN) [40].

2.4. Transient absorption spectroscopy

Transient absorption experiments were carried out on a nanosecond flash photolysis system that has been described previously [41]. Metal complex solutions were excited by using the third harmonic of an Nd:YAG laser (355 nm, 6 ns fwhm) with doses ranging from 2 to 15 mj/pulse. Calculated free ion yields were independent of pulse energy over this range. The yield of $PQ^{\cdot+}$ produced by electron transfer from the reduced (b)ReBP complexes was determined by extrapolation of the transient absorption at 605 nm to zero time and using the literature value for the extinction coefficient of $PQ^{\cdot+}$ ($\epsilon = 10060\ M^{-1}\ cm^{-1}$) [42]. Actinometry was effected by the 'relative actinometry method' by using the absorption of the MLCT excited state of (bpy)ReBP at 370 nm ($\Delta\epsilon = 11900 \pm 500\ M^{-1}\ cm^{-1}$) as a reference [43]. The unknown sample and (bpy)ReBP actinometer had matched absorption at 355 nm and the sample and actinometer were run in tandem to insure identical laser power and sample geometry.

3. Results

3.1. Electrochemistry and excited state quenching by DABCO

Cyclic voltammetry was carried out on each of the (b)ReBP complexes in CH_3CN solution with 0.1 M TBAH as a supporting electrolyte. Each complex displays a reversible cathodic wave that occurs at a potential that varies substantially with the diimine ligand. This wave is attributed to reduction of the coordinated diimine ligand (Eq. (1)) and the electrochemical potentials for the process ($E_{1/2}(b/b^{\cdot-})$) are listed in Table 1.

$$[(b)Re^{I}(CO)_3(BP)]^+ + e^- \longrightarrow [(b^{\cdot-})Re^{I}(CO)_3(BP)]^0 \qquad (1)$$

Photoexcitation of the (b)ReBP complexes in the near-UV region produces the triplet $d\pi\ (Re) \rightarrow \pi^*$ (diimine) MLCT excited state [37,38]. Emission from ^{3}MLCT is observed at wavelengths ranging from 550 to 700 nm depending upon the substituents on the diimine ligand [37,38]. Addition of DABCO to CH_3CN solutions of all of the (b)ReBP complexes leads to efficient quenching of the MLCT emission. Stern–Volmer lifetime quenching studies reveal that the quenching process is nearly diffusion controlled for each complex (k_q^{DABCO}, Table 1). The mechanism for MLCT quenching is attributed to photoinduced ET from DABCO to the photoexcited (b)ReBP complex (k_q^{DABCO}, Scheme 2). This hypothesis is supported by the previously reported excited state reduction potentials of the (b)ReBP complexes [37] and the experimentally determined oxidation potential of DABCO ($E_{1/2}(DABCO^{\cdot+}/DABCO) = +0.68$ V versus SCE), which in conjunction indicate that MLCT quenching by ET is exothermic by $\geqslant 0.4$ eV for each of the (b)ReBP complexes. Furthermore, the expected products of ET quenching are observed by transient absorption spectroscopy (vide infra).

3.2. Transient absorption studies

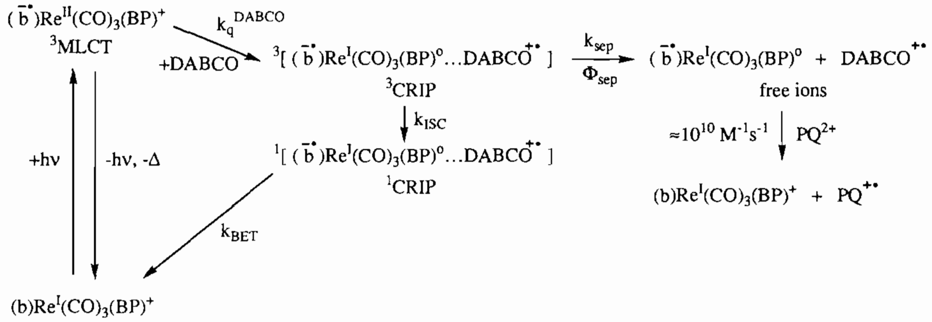
Nanosecond transient absorption (TA) spectroscopy was carried out on the (b)ReBP complexes to: (i) characterize the TA spectra of the MLCT excited states and the products formed by DABCO quenching; (ii) quantitatively determine the yields of free radical ions formed by ET quenching.

Pulsed nanosecond excitation (355 nm, 2–15 mj/pulse) of CH_3CN solutions of the (b)ReBP complexes leads to the appearance of TA spectra characteristic of the $d\pi\ (Re) \rightarrow \pi^*$ (diimine) ^{3}MLCT excited state. For example, the spectrum observed at 20 ns following laser excitation of (bpy)ReBP in CH_3CN is dominated by a moderately intense absorption at 370 nm (Fig. 1(a)). Similar features are observed in the TA spectra of MLCT states of other d^6 metal–bipyridine complexes; the strong near-UV transition is attributed to intraligand absorption of the diimine radical anion present in the MLCT state, $^*(b^{\cdot-})Re^{II}(CO)_3(BP)^+$ [44–46]. The difference molar absorptivity of the MLCT state of (bpy)ReBP was determined to be $\Delta\epsilon = 11900 \pm 500\ M^{-1}\ cm^{-1}$ at 370 nm by the relative actinometry method

Table 1
Electrochemical and electron transfer data for (b)ReBP complexes[a]

Ligand	$E_{1/2}(b/b^{\cdot-})$[b] (V)	τ_{em}[c] (ns)	k_q^{DABCO}[d] ($M^{-1}\ s^{-1}$)	ΔG_{BET}[e] (eV)	Φ_{sep}[f]	k_{BET}/k_{sep}
dmb	−1.24	257	9.4×10^9	−1.92	0.85 ± 0.01	0.18 ± 0.01
bpy	−1.16	224	9.5×10^9	−1.84	0.79 ± 0.02	0.26 ± 0.01
4-dab	−1.00	107		−1.68	0.73 ± 0.05	0.37 ± 0.02
5-dab	−0.92	31	1.0×10^{10}	−1.60	0.73 ± 0.05	0.37 ± 0.02
bpz	−0.64	27	1.2×10^{10}	−1.32	0.54 ± 0.05	0.85 ± 0.08

[a] All data in Ar-degassed CH_3CN solution.
[b] Half-wave potential for first (ligand-based) reduction relative to SCE reference.
[c] MLCT emission lifetime.
[d] Second-order rate constant for MLCT quenching by DABCO.
[e] Free energy for back ET in geminate radical pair; estimated error ±0.05 eV.
[f] Quantum yield for free ion formation.



Scheme 2.

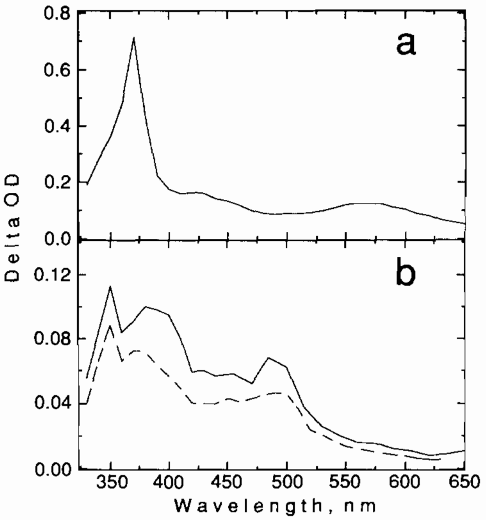


Fig. 1. Transient absorption spectra obtained following 355 nm pulsed excitation (5 mj, 6 ns fwhm). All samples in Argon degassed CH_3CN solution. (a) (bpy)RePyBz, $c=0.1$ mM, 20 ns delay; (b) dashed line: (bpy)RePyBz ($c=0.1$ mM) and DABCO ($c=100$ mM), 200 ns delay; solid line: (bpy)RePyBz ($c=0.1$ mM), DABCO ($c=100$ mM) and PQ^{2+} ($c=0.1$ mM), 0 ns delay.

by using triplet benzophenone as an actinometer [43][1]. Qualitatively similar transient absorption spectra were observed for the MLCT state in the other (b)ReBP complexes.

Transient absorption spectra were obtained for CH_3CN solutions of the (b)ReBP complexes with DABCO added at a concentration sufficient to quench ≥98% of the ^{3}MLCT [2]. The TA spectra indicated that in each case: (i) the MLCT state is completely quenched by DABCO during the nanosecond laser pulse; (ii) quenching produces moderately absorbing intermediates that are assigned to the free ions produced by ET quenching. For example, the dashed line in Fig. 1(b) is the spectrum observed at 200 ns delay following 355 nm excitation of a CH_3CN solution of (bpy)ReBP and DABCO. This spectrum is characteristic of the free ions formed by photoinduced ET quenching (Scheme 2): the near-UV features (350–400 nm) are attributed to the reduced metal complex, $[(bpy^{\bullet-})Re^{I}(CO)_3(BP)]^0$, and the band in the visible (450–500 nm) is due to the oxidized donor, $DABCO^{\bullet+}$ [47]. Consistent with assignment of the spectra to the separated free ions, the transient absorbance decays according to second-order equal concentration kinetics.

A TA technique was developed to quantitate the yield of free ions produced by photoinduced ET and cage escape from the geminate CRIP (Φ_{sep}, Scheme 2). The method is based on the approach used by Gould et al. to quantitate the yields of organic radical ions formed in bimolecular photoinduced ET reactions of aromatic D–A pairs [26]. Two pieces of information are required to determine Φ_{sep}: (i) the initial concentration of the MLCT excited state of (b)ReBP produced by the laser pulse (C_0^{MLCT}); (ii) the concentration of free ions produced by ET (C^{FI}). Assuming that [DABCO] is sufficient such that all of the MLCT state is quenched, Φ_{sep} is given by Eq. (2). C_0^{MLCT} was

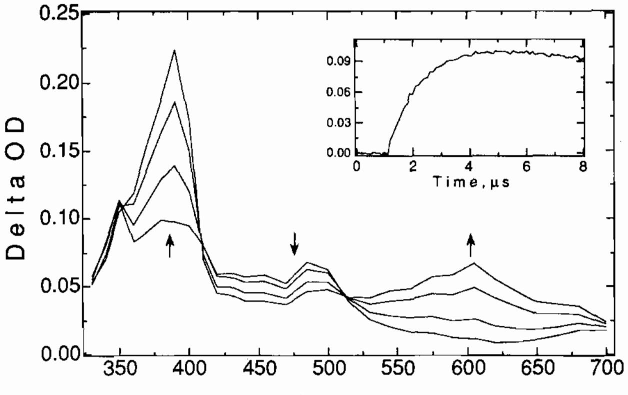


Fig. 2. Transient absorption spectra obtained following 355 nm pulsed excitation (5 mj, 6 ns fwhm). Main diagram: (bpy)RePyBz ($c=0.1$ mM), DABCO ($c=100$ mM) and PQ^{2+} ($c=0.1$ mM) in Ar degassed CH_3CN solution. Delay times: 0,80,160,240,480 and 800 ns. Arrows indicate direction of spectral change with increasing delay. Insert: transient absorption kinetics at 605 nm.

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[1] In the calculation of $\Delta\epsilon$ it is assumed that ^{3}MLCT is reached with unit quantum efficiency via intersystem crossing from ^{1}MLCT.

[2] The [DABCO] required to achieve ≥98% MLCT quenching was determined from the MLCT lifetime of the (b)RePB complex and k_q^{DABCO} (Table 1). Concentrations ranged from 20 mM for (dmb)ReBP to 200 mM for (bpz)ReBP.

$$\Phi_{\mathrm{sep}} = C^{\mathrm{FI}}/C_0^{\mathrm{MLCT}} \tag{2}$$

determined for each complex by the relative actinometry method using (bpy)ReBP as an external actinometer [43]. This approach operates under the assumption that C_0^{MLCT} for the unknown sample is the same as the concentration of MLCT excited state (bpy)ReBP produced by the laser. C^{FI} was determined by using [*N*,*N*′-dimethyl-4,4′-bipyridinium][PF_6^-]$_2$ (PQ^{2+}) as a secondary acceptor. PQ^{2+} was selected because it rapidly oxidizes the reduced (b)ReBP complexes producing $PQ^{\cdot +}$ and the Re^I complex in its initial oxidation state (Eq. (3)). Furthermore, $PQ^{\cdot +}$ has a strong absorption

$$[(b^{\cdot -})Re^I(CO)_3(BP)]^0 + PQ^{2+} \xrightarrow{\approx 10^{10} M^{-1}\ s^{-1}} [(b)Re^I(CO)_3(BP)]^+ + PQ^{\cdot +} \tag{3}$$

at 605 nm which is a region of the spectrum where there is little or no absorption due to the other radical ions produced by photoinduced ET.

Examples of the spectroscopic changes that occur upon application of a 355 nm pulse to a CH_3CN solution containing (bpy)ReBP ($c = 0.1$ mM), DABCO ($c = 100$ mM) and PQ^{2+} ($c = 0.1$ mM) are depicted in Figs. 1(b) and (2). First, the solid line in Fig. 1(b) illustrates the spectrum of this solution immediately following the laser pulse. This spectrum is nearly identical to that of a solution containing only (bpy)ReBP and DABCO (Fig. 1(b), dashed line) which indicates that since $[\mathrm{DABCO}] \gg [PQ^{2+}]$, only the former reacts with the MLCT excited state of (bpy)ReBP. Fig. 2 illustrates the temporal evolution of the spectrum of the (bpy)ReBP/DABCO/PQ^{2+} solution. Note that over a period of approximately 3 μs strong absorption develop at 394 and 605 nm (see inset, Fig. 2); these bands are clearly due to $PQ^{\cdot +}$ formed as shown by Eq. (3). The temporal evolution of the TA spectra for each of the other (b)ReBP complexes in the presence of DABCO and PQ^{2+} was qualitatively similar to that illustrated in Fig. 2.

The final calculation of Φ_{sep} for the (b)ReBP complexes was carried out using Eq. (4) where $A_{t=0}^{605\ \mathrm{nm}}$

$$\Phi_{\mathrm{sep}} = \frac{(A_{t=0}^{605\ \mathrm{nm}}/\epsilon_{605\ \mathrm{nm}}^{PQ^{\cdot +}})}{(A_{t=0}^{370\ \mathrm{nm}}/\Delta\epsilon_{370\ \mathrm{nm}}^{\mathrm{MLCT}})} \tag{4}$$

is the absorption at 605 nm extrapolated to zero time for the (b)ReBP/DABCO/PQ^{2+} solution, $\epsilon_{605\ \mathrm{nm}}^{PQ^{\cdot +}} = 10060\ M^{-1}\ cm^{-1}$ [42], $A_{t=0}^{370\ \mathrm{nm}}$ is the absorption at 370 nm at zero time for the (bpy)ReBP actinometer, and $\Delta\epsilon_{370\ \mathrm{nm}}^{\mathrm{MLCT}} = 11900\ M^{-1}\ cm^{-1}$. The calculated values of Φ_{sep} are collected in the final column of Table 1 and the values range from 0.54 (b = bpz) to 0.85 (b = dmb).

4. Discussion

4.1. Free energy dependence of BET in the CRIPs

The free energy change for BET in the organometallic CRIPs (ΔG_{BET}) is estimated by using the expression

$$\Delta G_{\mathrm{BET}} = E_{1/2}(\mathrm{DABCO}^{\cdot +}/\mathrm{DABCO}) - E_{1/2}(b/b^{\cdot -}) \tag{5}$$

where $E_{1/2}$ refers to the electrochemical half-wave potentials defined previously [1]. A coulombic interaction term is omitted in Eq. (5) because ET from neutral DABCO to the monovalent (b)ReBP complexes is formally a charge-shift reaction. By using the $E_{1/2}(b/b^{\cdot -})$ values listed in Table 1 along with $E_{1/2}(\mathrm{DABCO}^{\cdot +}/\mathrm{DABCO}) = +0.68$ V, ΔG_{BET} values for the series of (b)ReBP complexes are calculated using Eq. (5) (Table 1). Note that BET is strongly exothermic for each (b)ReBP complex, and assuming that the reorganization energy for this process is not unusually large, BET is likely to fall within the Marcus inverted regime [48].

According to the mechanism in Scheme 2, and assuming $k_{\mathrm{ISC}} \gg k_{\mathrm{BET}}$ (see below), the relationship between Φ_{sep} and the rate constants k_{BET} and k_{sep} is given by Eq. (6), which can be rearranged to Eq. (7). The latter expression reveals that the ratio $k_{\mathrm{BET}}/k_{\mathrm{sep}}$ is directly related to Φ_{sep}. Table 1 provides a tabulation of $k_{\mathrm{BET}}/k_{\mathrm{sep}}$ values for the (b)ReBP series calculated by using Eq. (7). Owing to the structural similarity of the (b)ReBP complexes, k_{sep} is anticipated to be

$$\Phi_{\mathrm{sep}} = k_{\mathrm{sep}}/(k_{\mathrm{sep}} + k_{\mathrm{BET}}) \tag{6}$$

$$k_{\mathrm{BET}}/k_{\mathrm{sep}} = [(1/\Phi_{\mathrm{sep}}) - 1] \tag{7}$$

relatively constant for the series; as a result, variation of the ratio $k_{\mathrm{BET}}/k_{\mathrm{sep}}$ provides a direct measure of the relative magnitude of k_{BET} for the complexes. With this in mind, the observed variation of $k_{\mathrm{BET}}/k_{\mathrm{sep}}$ as a function of ΔG_{BET} for the (b)ReBP series implies that k_{BET} decreases as ΔG_{BET} increases, in accord with expectations based on the semi-classical Marcus theory of highly exothermic ET processes [48]. However, despite the qualitative accord between the experimental results and predictions based on theory, there are several unusual features concerning the observed dependence of $k_{\mathrm{BET}}/k_{\mathrm{sep}}$ on ΔG_{BET} that will be highlighted and discussed in the succeeding sections.

4.2. Comparisons with related studies: mechanism of BET in organometallic CRIPs

Insight concerning the mechanism of BET in the $[(b^{\cdot -})Re^I BP^0 \ldots \mathrm{DABCO}^{\cdot +}]$ CRIPs can be gained by comparing the present results with those from studies of related systems. As noted above, Farid and Gould and co-workers studied geminate recombination in

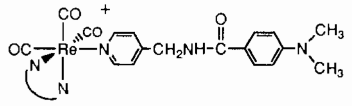
CRIPs formed by photoinduced bimolecular ET between organic D–A pairs [25–32]. In one case that is particularly relevant to the present study, Φ_{sep} was determined for singlet CRIPs formed by quenching the singlet excited state of the *N*-methylacridinium ion (+1) by alkylbenzene donors in CH_3CN [25]. (The charge type of BET in this system is the same as in the (b)ReBP/DABCO system). Interestingly, for BET reactions with $|\Delta G_{BET}| < 2.25$ eV, Φ_{sep} is < 0.05 in the acridinium/alkylbenzene system. By contrast, in the (b)ReBP/DABCO system Φ_{sep} is substantially larger, even for a smaller driving force. The larger ϕ_{sep} for (b)ReBP/DABCO CRIPs is very likely due to the fact that ET from DABCO to ^{3}MLCT of (b)ReBP initially produces a triplet CRIP (^{3}CRIP, Scheme 2). In this case, intersystem crossing (ISC) to form ^{1}CRIP must occur prior to BET, and this added step increases the lifetime of the CRIP thereby increasing the probability for cage escape and formation of free ions.

Another interesting comparison arises upon consideration of results from studies by Hoffman, Ohno and co-workers in which Φ_{sep} values were determined for CRIPs formed by oxidative quenching of the ^{3}MLCT state of a series of Ru(II)–polypyridyl complexes by PQ^{2+} as shown in Eq. (8) [33, 34]. In this study the

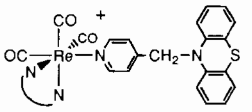
$$^{*}\mathrm{Ru}^{II} + \mathrm{PQ}^{2+} \longrightarrow [\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{\cdot+}] \xrightarrow{\Phi_{sep}} \mathrm{Ru}^{III} + \mathrm{PQ}^{\cdot+} \qquad (8)$$

dependence of Φ_{sep} on ΔG_{BET} was examined over the range -2.0 to -1.4 eV, which overlaps the range explored in the present study. The unusual feature is that Φ_{sep} for the $[\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{\cdot+}]$ CRIPs fall in the range 0.1–0.2, which is substantially lower than observed for the $[(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}\mathrm{BP}^{0}\ldots\mathrm{DABCO}^{\cdot+})]$ CRIPs. This difference could stem from either of two factors that differ for the two systems: (i) k_{sep} is smaller for the $[\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{\cdot+}]$ CRIPs; (ii) at comparable ΔG_{BET}, k_{BET} is larger in the $[\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{\cdot+}]$ CRIPs. First, it is very unlikely that k_{sep} is smaller for the $[\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{\cdot+}]$ CRIPs owing to the fact that in this ion-pair, coulombic repulsion between Ru^{3+} and PQ^{1+} should lead to a larger k_{sep} compared to that for the $[(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}\mathrm{BP}^{0}\ldots\mathrm{DABCO}^{\cdot+}]$ CRIPs where there is little or no coulombic repulsion between the ions. Moreover, Hoffman has demonstrated that Φ_{sep} for $[\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{\cdot+}]$ CRIPs decreases with increasing ionic strength, consistent with the hypothesis that coulombic repulsion between the ions accelerates k_{sep} relative to that for ions that do not have like charge [33]. With this in mind, it seems likely that the difference in Φ_{sep} for the two systems is due to the fact that k_{BET} is considerably larger in the $[\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{\cdot+}]$ CRIPs.

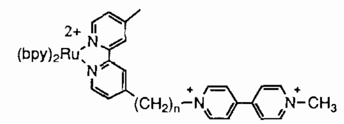
The qualitative difference in k_{BET} for CRIPs formed by oxidative quenching (e.g. $[\mathrm{Ru}^{III}\ldots\mathrm{PQ}^{1+}]$) and reductive quenching (e.g. $[(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}\mathrm{BP}^{0}\ldots\mathrm{DABCO}^{\cdot+}]$) of d^6 metal complexes is mirrored by results obtained for *intramolecular* BET in covalently linked molecules that have analogous structural features [16–18]. For example, at comparable driving force k_{BET} is 10^2–10^3 times greater in the charge-separated state, Ru^{III}–$(\mathrm{CH}_2)_n$–$\mathrm{PQ}^{\cdot+}$, formed by photoexcitation of Ru–$(\mathrm{CH}_2)_n$–PQ^{2+} compared to k_{BET} for the charge-separated states, $(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}(\mathrm{CO})_3$–$(\mathrm{Py}$–$\mathrm{D}^{\cdot+})$, formed by photoexcitation of either of the donor-substituted complexes (b)RePy–PTZ or (b)RePy–DMAB [14,18,21].



(b)RePy-DMAB



(b)RePy-PTZ



Ru-(CH$_2$)$_n$-PQ^{2+}

Prior to discussion of the possible origin of this effect, it is important to note that BET in either the inter- or intramolecular Ru^{III}--$\mathrm{PQ}^{\cdot+}$ systems involves transfer of an electron that is localized on the organic $\mathrm{PQ}^{\cdot+}$ donor to an electron hole that is localized largely within a dπ orbital at the d^5 metal center. By contrast, BET in either the inter- or intramolecular $(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}(\mathrm{CO})_3$--donor$^{\cdot+}$ systems involves transfer of an electron that is localized in a π^* MO on the diimine ligand to an electron hole that is localized in a π MO on the organic donor ligand. In other words, with respect to the basis set of orbitals involved, BET in the $(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}(\mathrm{CO})_3$--donor$^{\cdot+}$ systems is essentially a highly exothermic charge recombination between an organic radical anion donor and an organic radical cation acceptor that are in proximity to a d^6 metal center.

With this in mind, one explanation for the lower k_{BET} in the $(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}(\mathrm{CO})_3$--donor$^{\cdot+}$ systems compared to the Ru^{III}--$\mathrm{PQ}^{\cdot+}$ systems is that triplet–singlet ISC in the charge-separated states is much faster in the latter case, owing to the fact that a substantial fraction of the unpaired spin density is in a dπ orbital at the d^5 Ru^{III} center. In the $(\mathrm{b}^{\cdot-})\mathrm{Re}^{I}(\mathrm{CO})_3$--donor$^{\cdot+}$ systems, triplet–singlet ISC may be slowed owing to the fact that the electron and hole are in orbitals primarily localized on the organic ligands; in effect the d^6 Re center acts to only moderately enhance ISC by acting as an ‘external heavy atom’. In fact, evidence presented below implies that in the $(b^{\bullet -})Re^I(CO)_3$--donor$^{\bullet +}$ systems ISC may be so slow such that it is the rate determining step for decay of the charge-separated states in both the inter- and intramolecular systems (e.g. $k_{ISC} < k_{BET}$).

Finally, a very interesting correlation arises upon comparing the dependence of k_{BET} on ΔG_{BET} for the $[(b^{\bullet -})Re^I BP^0 \ldots DABCO^{\bullet +}]$ CRIPs examined in the present study with that observed for intramolecular BET in the two series of donor-substituted Re^I complexes, (b)RePy–DMAB and (b)RePy–PTZ [14,21]. For the purposes of this comparison, k_{BET} values for the $[(b^{\bullet -})Re^I BP^0 \ldots DABCO^{\bullet +}]$ CRIPs were estimated from the experimental values of k_{BET}/k_{sep} (Table 1) by assuming $k_{sep} = 5 \times 10^8$ s^{-1}. Previous studies indicate that this is an excellent assumption [49]; however, it is important to note that even though the approximation may not provide correct absolute values of k_{BET}, the choice of k_{sep} has no influence on the slope of a log (k_{BET}) versus ΔG_{BET} correlation.

Fig. 3 illustrates a comparision of the correlation between log (k_{BET}) and ΔG_{BET} for the three $(b)Re^I(CO)_3$--donor systems. Two features are striking in this correlation. First, as noted in a previous report, the absolute rate data for the two covalently linked systems follow virtually the same correlation [37]. This seems somewhat remarkable in view of the fact that in these two systems the donors and the linkers have substantially different structure. Studies of ET in a variety of covalently linked systems indicate that even subtle structural changes in the spacer or the molecular structure of the donor or acceptor often have a substantial effect on the magnitude of the D–A electronic coupling, and therefore on k_{ET} [6,7,50,51]. The second striking feature in Fig. 3 is the close correspondence between the slope of the log (k_{BET}) versus ΔG_{BET} correlation for the inter- and intramolecular systems. Furthermore, although the absolute values of k_{BET} for the intermolecular system are estimated, it seems remarkable that the correlation for k_{BET} in the CRIPs is not displaced substantially from that for the covalently linked compounds.

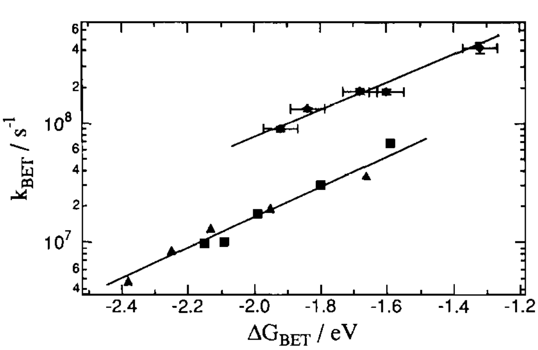
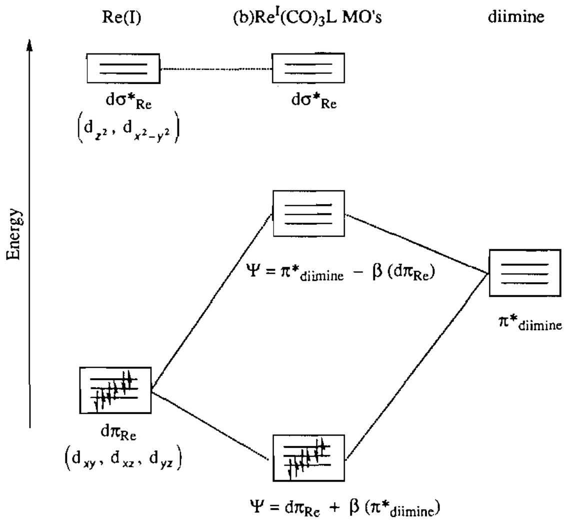


Fig. 3. Plot of k_{BET} vs. ΔG_{BET} in CH_3CN for three $(b)Re(CO)_3$--donor systems. Polygons with error bars are data for BET in $[(b^{\bullet -})Re^I BP^0 \ldots DABCO^{\bullet +}]$ CRIPs (this work); triangles are data for the (b)RePy–DMAB system [21]; squares are data for the (b)RePy–PTZ system [14].

If it is assumed that BET in both the inter- and intramolecular $(b)Re^I(CO)_3$--donor systems is controlled by the intrinsic rate of ET (e.g. $k_{obs} = k_{BET}$), the correlations in Fig. 3 would indicate that: (i) the donor–acceptor electronic coupling (V_{el}) in all three systems differs by less than a factor of 3; (ii) the inner- and outer-sphere reorganization energy (λ) is virtually identical in all three systems. Both of these points seem rather remarkable. First, detailed studies indicate that V_{el} is comparatively low, and therefore ET is non-adiabatic in the covalently linked compounds (b)RePy–PTZ and (b)RePy–DMAB [14,21]. This is not surprising given that the spacers cannot adopt conformations that allow the donor and acceptor ligands to come into close proximity in these complexes [14,21]. By contrast, in the $[(b^{\bullet -})Re^I BP^0 \ldots DABCO^{\bullet +}]$ CRIPs, the donor and acceptor should be able to come into very close proximity allowing V_{el} to be substantially larger than in the covalently linked compounds. However, this is not manifest in the experimental data, for at comparable ΔG_{BET} the observed rates for the CRIPs are not markedly faster than in the covalently linked compounds (see Fig. 3). Furthermore, while λ for the inter- and intramolecular systems is not expected to be dramatically different, the correlations in Fig. 3 imply that it is virtually identical.

Taken together, the experimental data for the three $(b)Re^I(CO)_3$--donor systems strongly imply that the rate determining step for BET in these systems is triplet–singlet ISC in the charge-separated state (e.g. $k_{obs} = k_{ISC}$). If this is the case, then the correlation between the observed rate and ΔG_{BET} must result from a systematic relationship between the redox potential of the diimine ligand ($E_{1/2}(b/b^{\bullet -})$) and k_{ISC}.

A rational explanation for this effect is as follows (refer to the MO energy level diagram shown in Scheme 3). In the charge-separated state for either the inter- or intramolecular $(b)Re^I(CO)_3$--donor systems, the odd electron occupies an MO that can be represented as $\Psi = [\pi^*_{diimine} - \beta(d\pi_{Re})]$ (where Ψ, π^* and $d\pi$ represent MO wavefunctions and β is a scalar coefficient). Since the energy of $\pi^*_{diimine}$ (ϵ_{π^*}) is greater than that of $d\pi_{Re}$, perturbation theory indicates that β decreases as ϵ_{π^*} increases (or as $E_{1/2}(b/b^{\bullet -})$ becomes more negative). Therefore, in the charge-separated state for all $(b)Re^I(CO)_3$--donor systems, the odd electron occupies an orbital that has increasing $d\pi_{Re}$ character as $E_{1/2}(b/b^{\bullet -})$ becomes less negative. The expected cor-



Scheme 3.

relation between $k_{\rm ISC}$ and $E_{1/2}$(b/b$^{\bullet-}$) can now be explained by using this orbital model. It is reasonable to expect that $k_{\rm ISC}$ will increase as β increases, because spin–orbit coupling should increase as the degree of metal character in the MO which the odd electron occupies increases. Now, since β increases as $E_{1/2}$(b/b$^{\bullet-}$) becomes less negative, it follows that $k_{\rm ISC}$ in the charge-separated state in the (b)Re^I(CO)$_3$--donor systems will increase as $E_{1/2}$(b/b$^{\bullet-}$) becomes less negative. This predicted trend is in accord with the experimentally observed values of '$k_{\rm BET}$' in all of the (b)Re^I(CO)$_3$--donor systems that have been examined to date [14,21].

5. Conclusions

A transient absorption technique has been developed and used to determine the cage escape efficiency for CRIPs formed upon photoinduced ET from DABCO to a series of (b)ReBP complexes. The dependence of $\Phi_{\rm sep}$ on $\Delta G_{\rm BET}$ for the organometallic CRIPs implies that the rate of BET decreases as the process becomes more exothermic. Comparison of the rate data for the (b)ReBP/DABCO system with that for highly exothermic charge recombination reactions in other inter- and intramolecular systems leads to several significant conclusions regarding BET in (b)Re(CO)$_3$--donor systems. (i) The initial charge-separated state in these systems retains triplet spin character. (ii) The remarkable correspondence between rate data for three unique (b)Re(CO)$_3$--donor systems strongly implies that the rate determining step for decay of the charge-separated states is triplet–singlet ISC, not the intrinsic rate of BET. Studies in progress are using time resolved ESR to examine the dynamics of ISC in the charge-separated state of covalently linked (b)Re(CO)$_3$--donor compounds.

Acknowledgement

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