Photophysics and photochemistry of triplet exciplexes between triplet naphthalene derivatives and benzophenone

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Abstract: The photophysical and photochemical behaviors in the naphthalene derivatives (RX) and benzophenone (BP or >CO) systems have been studied by means of 355-nm laser photolysis techniques in polar media. At the initial event, the triplet energy transfer (TET) occurs from ^{3}BP* to RX in the nanosecond region. It is found that the following reactions occur effectively in polar media via the triplet exciplexes having loose sandwich-like structures with weak charge-transfer character in the microsecond region: (1) For RNH$_3^+$-BP or ROH-BP system, hydrogen atom transfer (HT), for the latter proton-enhanced HT whereas for the former proton-reduced HT, and the more protic hydrogen atom of -NH$_3^+$ is more reactive in HT for the HORNH$_3^+$-BP system (2) for the ROMe-BP system, proton-induced electron transfer (ET) in the presence of protons. (3) for the RN(Me)$_2$ (or RN(Et$_2$))-BP system, hydrogen-bonding-induced ET in the presence of H$_2$O or methanol.

1. INTRODUCTION

Since the first report on the triplet sensistization of naphthalene by benzophenone in a rigid matrix by Terenin and Ermolaev (ref.1), a large number of studies on triplet energy transfer have been reported (refs.2-4). However, little attention has been paid to the interactions of triplet-sensitized compounds with the ground state of triplet energy donors until recently. In this decade, we have been interested in photophysical and photochemical behaviors in the triplet aromatic compounds (especially for naphthalene derivatives) and benzophenone by means of laser photolysis techniques at 355 nm (ref.5-15). It has been found that new types of photochemical reactions such as hydrogen atom transfer (HT) (refs.5,7-10,13,14) proton-enhanced HT (refs.9,10), proton-induced electron transfer (ET) (ref.6,10,11,14), and hydrogen-bonding induced ET (ref.15) take place effectively via triplet exciplexes having loose sandwich-like structures with weak CT character (ref.7-15). Upon dircect excitation, it is well-known that naphthol or naphthylammonium ion undergoes proton transfer in the excited singlet state (S$_1$) (ref.16), while in the triplet state (T$_1$) HT takes place effectively. This may be due to the difference in the electronic structures between S$_1$ and T$_1$ states, the former is ionic and the latter biradical-like. The proton effects on the triplet exciplexes have been revealed to be remarkable as well as those on the S$_1$ state where proton-induced quenching (chemical quenching) takes place (refs.16-18). Even in the case of no photochemical reaction in T$_1$, it has been also shown that the triplet molecules sensitized by ^{3}BP* decay via the triplet exciplexes (ref. 19). Here, the photophysical and photochemical processes of triplet naphthalene derivatives with BP studied by laser photolysis techniques at 355 nm are described.

2. RESULTS AND DISCUSSION

2.1 Hydrogen atom transfer from 2-naphthlylammonium ion to BP (ref.8)

The laser flash photolysis study at 355 nm in the 2-naphthylammonium ion (RNH_3^+) and benzophenone (BP) system has been carried out in methanol-water (9:1 v/v) at 290 K. At first, triplet benzophenone ($^3BP^*$) produced by fast intersystem crossing of $^1BP^*$ excited at 355nm is quenched by RNH_3^+ with almost diffusion-controlled rates (1.1×10^{10} M^{-1} s^{-1} at $[H_2SO_4]$ = 0.015 M; 3.9×10^9 M^{-1} s^{-1} at $[H_2SO_4]$ = 0.5 M). The triplet 2-naphthylammonium ion ($^3RNH_3^{+*}$) with a peak at 410 nm is produced in the nanosecond resion by TET from $^3BP^*$ (with a peak at 525 nm) to RNH_3^+ with efficiencies of 0.41 ($[H_2SO_4]$ = 0.015 M) and 0.33 ($[H_2SO_4]$ = 0.5 M) at $[RNH_3^+]$ = 3.0×10^{-3} M and at [BP]=1.2×10^{-2} M, competing with hydrogen abstraction from solvent (methanol) or RNH_3^+ molecules. Subsequently, in the microsecond time scale the hydrogen atom transfer (HT) reaction from $^3RNH_3^{+*}$ (410 nm) to ground BP occurs effectively to give naphthylamine cation radical ($RNH_2^{·+}$, 510 nm) and the benzophenone ketyl radical ($>\dot{C}OH$, 545 nm) as shown in Fig. 1. The decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ increases with an increase of the BP concentration, and at higher BP concentrations a leveling off is observed. The $(\tau_{obsd})^{-1}$ value decreased drastically with an increase of acid concentration. The mechanism of the HT reaction can be accounted for by the intracomplex HT reaction of the triplet exciplex $^3(RNH_3^+\cdots>CO)^*$ with a rate constant of ca. 5×10^6 s^{-1}. At higher acid concentrations, the triplet exciplex is decomposed by protonation to the triplet exciplex to
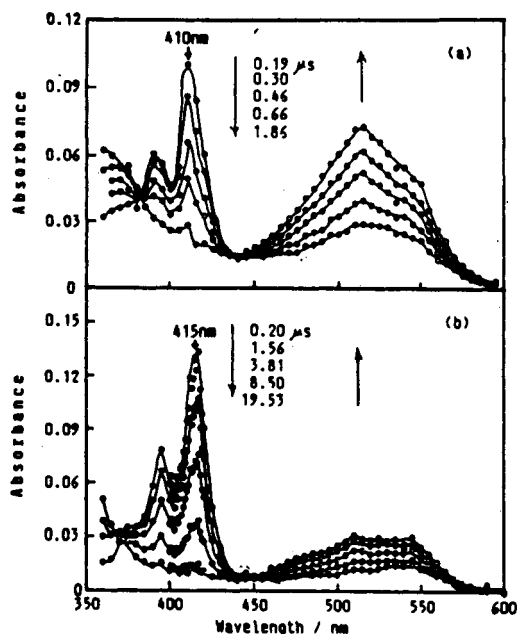

Fig. 1 Time-resolved transient absorption spectra of the $[RNH_3^+]$ = 3.0×10^{-3} M and [BP] = 1.12×10^{-2} M system on the microsecond time scale in the presence of 0.015 (a) and 0.5 M (b) H_2SO_4, obtained by laser flash photolysis at 355 nm.
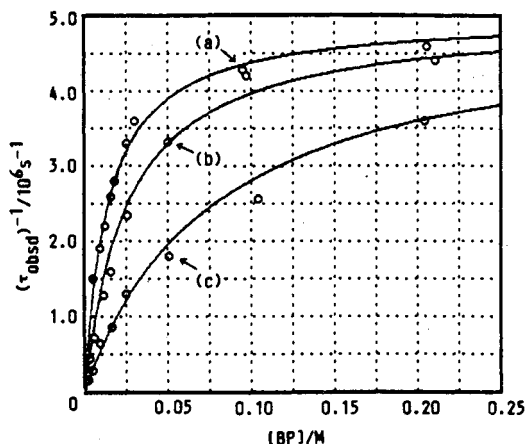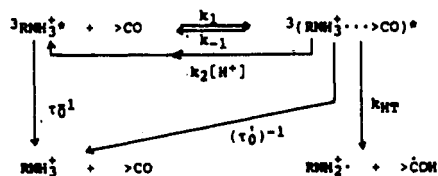

Fig. 2 Plots of the decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ as a function of [BP] monitored at 410 nm in the presence of 0.015 (a), 0.05 (b), and 0.2 M H_2SO_4 (c). The solid curve denotes the calculated one from eq 7, which agrees with the experimental data. For details, see text.

Scheme 1

where $(\tau')^{-1} = k_{HT} + (\tau_0')^{-1}$ and $K_1 = k_1/k_{-1}$

give free $^3RNH_3^{+*}$ and BP, resulting in suppresion of the rate for the HT reaction (Fig.2). Therefore, the HT reaction from $^3RNH_3^+$ to BP (>CO) can be expressed by Scheme 1, where K_1 = 110 M^{-1} k_2/k_1 = 40 M^{-1}, τ_0^{-1} = 1×10^4 s^{-1}, $(\tau')^{-1}$ = 5×10^6 s^{-1}, and $k_{HT} ≈ \tau')^{-1}$. The decay rate $(\tau_{obsd})^{-1}$ in the $HClO_4$ system was the same as that of H_2SO_4 system indicating that H_2SO_4 acts as a monobasic acid in a methanol-water (9:1 v/v) mixture. No effect of the counter anion SO_4^{2-} on k_{HT} was confirmed. At a lower acid concentration (0.015 M), the efficiency for HT was evaluated as 0.95.

2.2   Hydrogen atom transfer from 1-naphthol to BP and proton-enhanced hydrogen atom transfer (refs.7,9)

The laser flash photolysis in the 1-naphthol (ROH) and benzophenone (BP) system with and without H_2SO_4 has been carried out in acetonitrile-water (4:1 v/v) or methanol at 290K. For the ROH (3.0×10^{-3} M)-BP(6.7×10^{-3} M) system containing $[H_2SO_4] = 0$ or 0.5M in acetonitrile-water (4:1 v/v), $^3BP^*$ produced fast intersystem crossing of $^1BP^*$ excited at 355 nm is quenched by ROH with almost diffusion processes (8.4×10^9 or $9.3 \times 10^9 M^{-1} s^{-1}$, respectively) involving TET, hydrogen abstraction and induced quenching processes (ref.20). Triplet naphthol ($^3ROH^*$) is produced in the nanosecond region by TET from $^3BP^*$ to ROH with efficiencies 0.73 and 0.39 for $[H_2SO_4] = 0$ and 0.5 M, respectively. Subsequently, in the microsecond reion, the HT reaction from $^3ROH^*$ to BP occurs to yield the 1-
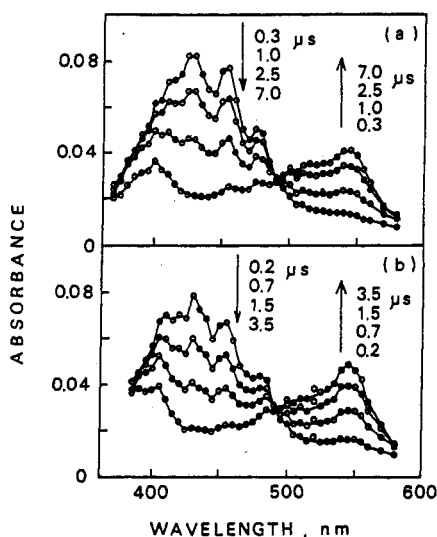

Fig. 3 Time-resolved transient absorption spectra of the ROH (3.0 $\times 10^{-3}$ M)-BP (6.7 $\times 10^{-3}$ M) system in acetonitrile-water (4:1 v/v) in a microsecond region for $[H_2SO_4] = 0$ M (a) and 0.5 M (b) observed after 355-nm laser pulsing at 290 K.

naphthoxy radical (RO·) and >ĊOH with efficiencies 0.73 and 0.85 for $[H_2SO_4] = 0$ and 0.5M, respectively. Fig. 3 shows the transient absorption spectra observed at 0.2-7.0 μs after laser pulsing in ROH (3.0×10^{-3}M)-BP(6.7×10^{-3}M) system containing (a) $[H_2SO_4] = 0$ and (b) 0.5 M in acetonitrile-water (4:1 v/v) at 290 K. In both spectra (a) and (b), the 430 nm band for $^3ROH^*$ decreases with an isosbestic point at 490nm, accompanying an increase in intensities of the 545 nm and the 400 nm bands for >ĊOH and RO·, respectively. In contrast to the case of the RNH_3^+-BP system (ref.8), the rate constant for the decay of $^3ROH^*$ (k_{obsd}) linearly increases with an increase of $[H_2SO_4]$. As for an increase of [BP], the value of k_{obsd} increases nonlinearly which shows a negative curve both in systems with and without H_2SO_4. Especially for the methanol solution with $[H_2SO_4] = 0$ M, a leveling off is clearly observed at higher [BP] (> 0.5 M). In the absence of H_2SO_4, the HT mechanism from $^3ROH^*$ to BP can be explained by the intraexciplex HT reaction of the triplet exciplex ^{3}(ROH···>CO)* with an equilibrium constant $K_1 = 6.7 M^{-1}$ in acetonitrile-water (4:1 v/v) or 4.2 M^{-1} in methanol. The mechanism of the proton-enhanced HT reaction is suggested that the protonated triplet exciplex ^{1}(ROH···>ĊOH)* formed in a prototropic equilibrium with ^{3}(ROH···>CO)* undergoes the intraexciplex electron-transfer reaction to give the triplet radical pair ^{3}(ROH·$^+$··· >ĊOH) which rapidly decomposes into RO· + >ĊOH + H$^+$.

2.3.   Proton-induced electron transfer reaction from triplet methoxynaphthalenes to BP (ref.10)

A laser photolysis study at 355 nm has been carried out on acetonitrile-water (4:1 v/v) mixtures of the methoxynaphthalene (ROMe)-BP-H_2SO_4 system. It is found that the proton-assisted photoionization reaction of triplet 1- and 2-ROMe produced by triplet sensitization of BP effectively occurs to produce the corresponding cation radical ROMe·$^+$ and> ĊOH . The TET reaction from $^3BP^*$ to ROMe takes place as the primary event to produce $^3ROMe^*$ and BP. The 1:1 triplet exciplex ^{1}(ROH···>CO)* having a weak charge-transfer structure is readily formed between $^3ROMe^*$ and BP with K_1 (10.1 M^{-1} for 1-ROMe, 4.0 M^{-1} for 2-ROMe at 290 K). In the presence of protons, the triplet protonated exciplex ^{3}(ROMe··· >ĊOH) * is
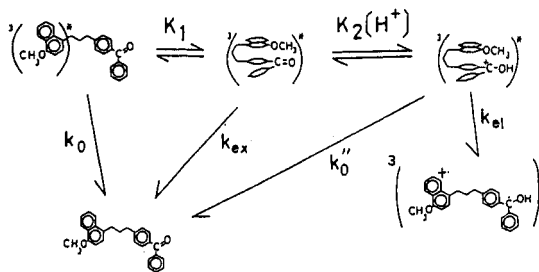
formed by protonation to $^3(ROMe \cdots >CO)*$. Subsequently, the intraexciplex electron-transfer (ET) reaction takes place effectively in $^3(ROMe \cdots > \overset{+}{C}OH)*$, resulting in the formation of $ROMe^{\cdot+}$ and $>\overset{\cdot}{C}OH$ as shown in Fig. 4. The electron affinity of the protonated BP ($>\overset{+}{C}OH$) in the exciplex may become large compared to that of BP resulting in the intraexciplex ET. In the absence of protons, ^3ROMe decays via $^3(ROMe \cdots >CO)*$ to the ground ROMe and BP.

2.4. Intramolecular hydrogen atom transfer of [(hydroxynaphthyl)propyl]benzophenone and intramolecular proton-induced electron transfer of [(methoxynaphthyl)propyl] benzophenone via triplet exciplexes (ref.11)

Laser photolysis studies at 355 nm have been carried out on the intramolecular HT reaction of
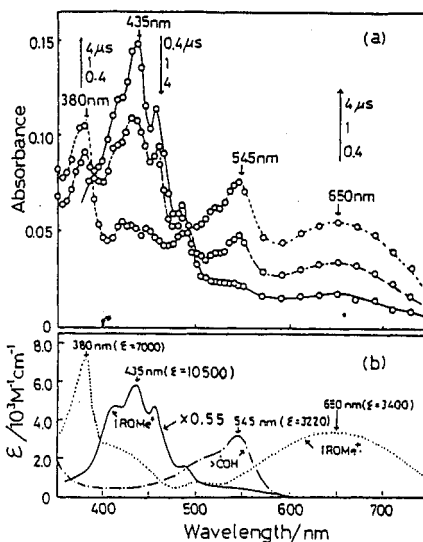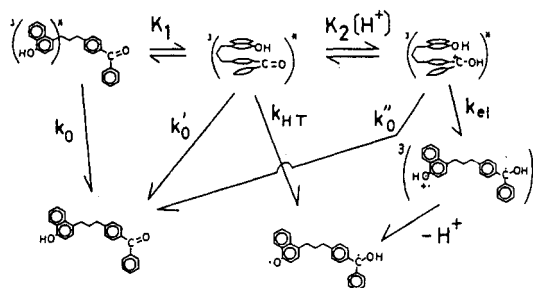

Fig. 4 (a) Time-resolved transient absorption spectra in a microsecond time scale for the 1ROMe (3.0 × 10⁻³ M)-BP (6.7 × 10⁻³ M)-H₂SO₄ (1.0 M) system in acetonitrile-water (4:1 v/v) observed after 355-nm laser pulsing at 290 K. (b) Reference absorption spectra for the transient species (³1ROMe*, >ĊOH, and 1ROMe⁺).

BP-$(CH_2)_3$-ROH and the proton-induced intramolecular ET of BP-$(CH_2)_3$-ROMe in acetonitrile-water (4:1 v/v) at 295K. At the primary event, intramolecular TET from $^3BP*$ moiety to ROH or ROMe moiety occurs to yield BP- or BP-$(CH_2)_3$-$^3ROMe*$ very rapidly. Subsequently, BP-$(CH_2)_3$-$^3ROH*$ undergoes intramolecular HT to yield $>\overset{\cdot}{C}OH$-$(CH_2)_3$-RO· with a rate constant of 9.8×10^5 s⁻¹ (5.1×10^5 s⁻¹ for BP-$(CH_2)_3$-$^3ROD*$) as shown in Scheme 2. The intramolecular HT is enhanced by protons. The BP-$(CH_2)_3$-$^3ROMe*$ undergoes the intramolecular proton-induced ET reaction to give $>\overset{\cdot}{C}OH$-$(CH_2)_3$-$ROMe^{\cdot+}$ (Scheme 3). On the basis of the mechanisms for intramolecular HT and proton-induced ET of the two chromophores linked with a propylene chain, the structures of the triplet exciplex and protonated triplet exciplex are suggested to be sandwich-like with weak CT character.

Scheme 2

Scheme 3

2.5. Hydrogen atom transfer from the triplet hydroxynaphthylammonium ion to BP via a triplet exciplex. Which group is more reactive for hydrogen atom transfer, -OH or -NH₃⁺? (ref.13)

Laser flash photolysis studies on HT from 5-aminonaphth-1-ol (HORNH₃⁺) to BP in methanol-water (9:1 v/v) at 295 K have been carried out in order to elucidate which hydrogen atom of the substituent groups is more reactive for HT, and what is the

mechanism. It was found that HT from $^3HORNH_3^{+*}$ produced by TET from $^3BP^*$ to BP occurs to yield $HORNH_2^{\cdot+}$ and $> \dot{C}OH$ with efficiencies of 0.92 and 0.48 in the presence of 0.015 and 0.5 M H_2SO_4, respectively. The decay rate of $^3HRONH_3^{+*}$ (k_{obsd}) decreased with increasing acid concentration, approaching to a constant value at higher acid concentrations. This fact shows that the HT reaction results from the proton-induced ET followed by proton dissociation at higher acid concentrations.

2.6. Thermochemical profiles on hydrogen atom transfer and proton-induced electron trasnfer reactions via triplet exciplexes. (ref.14)

Themperature effects on HT and proton-induced ET via triplet explexes in the ROH-BP ,and ROMe -BP systems in acetonitrile-water (4:1 v/v) have been studied by 355nm laser flash photolysis. The HT rate in the ROH-BP system increased with increasing temperature. The thermodynamic parameters for HT via $^3(ROH\cdots>CO)^*$ were obtained: the enthalpy change, $\Delta H_1 = -2.0$ kcal mol^{-1} and entropy change, $\Delta S_1 = -2.4$ eu for the formation of $^3(ROH\cdots>CO)^*$; the frequency factor, $A_{ex} = 7.7 \times 10^9 s^{-1}$ and activation energy = 3.5 kcal mol^{-1}, for HT. The negatively small values of ΔH_1 and ΔS_1 suggest that $^3(ROH\cdots>CO)^*$ has a loose sandwich-like structure. The corresponding parameters in the ROMe-BP system were obtained to be $\Delta H_1 = -2.2$ kcal mol^{-1} and $\Delta S_1 = -2.8$ eu for the formation of $^3(ROMe\cdots>CO)^*$. Both the rates for proton-induced HT and ET increased with increasing temperature.

2.7. Hydrogen-bonding-induced electron transfer from triplet N,N-dialkylamines to benzophenone via triplet exciplexes (Ref.15)

Laser photolysis studies in the BP and N,N-dialkyl-1-naphthylamine, DANA (N,N-dimethyl-1-naphthylamine, $RN(Me)_2$ and N,N-diethyl-1-naphthylamine, $RNEt_2$) system have been carried out in acetonitrile with and without H_2O (or methanol) at 295K. In the nanosecond time scale, TET from $^3BP^*$ to DANA occurs with the efficency ϕ_{TET} (0.74 for $RNMe_2$ and 0.61 for $RN(Et)_2$) regardless of the presence of H_2O or methanol. After the formation of $^3DANA^*$, $^3(DANA\cdots BP)^*$ with weak CT character is produced with K_1 ($10 M^{-1}$ for $RN(Me)_2$ and 9 M^{-1} for $RN(Et)_2$) between $^3DANA^*$ and BP. In the presence of H_2O or methanol, it was found that the intraexciplex ET takes place to give the BP anion ($>CO^{\cdot-}$) and DANA cation ($DANA^{\cdot+}$) radicals in the hydrogen-bonded triplet exciplex $^3(DANA\cdots>CO)^*_{HB}$ by H_2O or methanol. The equilibrium constants K_2 for the formation of $^3(DANA\cdots>CO)^*_{HB}$ with H_2O and methanol obtained are 0.55 and 0.45 M^{-1} for DMNA, 0.50 and 0.40 M^{-1} for DENA. The rate constants k_{et} for ET induced by hydrogen-bonding were determined to be $2.5 \times 10^7 s^{-1}$ for $RN(Me)_2$ and 1.4×10^7 s^{-1} for $RN(Et)_2$. It was revealed that the driving force for ET is the negatively enlarged reduction potential of BP in $^3(DANA\cdots>CO)^*_{HB}$ due to the hydrogen bonding to the carbonyl group of BP in $^3(DANA\cdots>CO)^*$.

3. CONCLUDING REMARKS

Laser flash photolysis studies at 355 nm on the photophysical and photochemical features in the naphthalene derivatives (RX) and benzophenone (BP or >CO) have been carried out in polar media. The triplet energy transfer (TET) from $^3BP^*$ to RX takes place in the nanosecond region at the primary event. After TET, the triplet exciplexes $^3(RX\cdots>CO)^*$ having loose sandwich-like structures with weak CT character are produced resulting in the following reactions in the microsecond time scale.

(1) In the $BP\text{-}RNH_3^+$ or BP-ROH system, hydrogen atom transfer (HT) occurs effectively via the triplet exciplex $^3(RNH_3^+\cdots>CO)^*$ or $^3(ROH\cdots>CO)^*$ to yield $RNH_2^{\cdot+}$ and $> \dot{C}OH$ or $RO\cdot$ and $> \dot{C}OH$ respectively. The HT reaction for the former is reduced significantly in the presence of protons, whereas

for the latter is enhanced. The proton-enchanced HT results from the intracomplex electron transfer (ET) of the protonated triplet exciplex ^{3}(ROH$\cdots$> $\overset{+}{C}$OH)* followed by proton dissociation.

(2) In the BP-ROMe system, proton-induced ET takes place to yield ROMe$^{\cdot+}$ and > $\dot{C}$OH via the intraexciplex ET of ^{3}(ROMe$\cdots$> $\overset{+}{C}$OH)* in the presence of protons.

(3) The two chromophores (BP and ROH or BP and ROMe) linked with a propylene chain undergo effectively intramolecular HT or proton-induced ET to yield > $\dot{C}$OH -(CH$_2$)$_3$-RO· or > $\dot{C}$OH -(CH$_3$)$_3$-ROMe$^{\cdot+}$, respectively. This fact indicates that the triplet exciplexes have sandwich-like structures with weak CT character.

(4) The temperature effects on the triplet exciplex formation show that the triplet exciplex has a loose sandwich-like structure with CT character.

(5) For the naphthalene derivative HORNH$_3^+$ having both -OH and NH$_3^+$ groups and BP system, HT occurs via the triplet exciplex to give HORNH$_2^{\cdot+}$ and > $\dot{C}$OH. This fact means that the more protic hydrogen atom is the more reactive in HT via the triplet exciplex.

(6) Hydrogen-bonding-induced ET is found via the hydrogen bonded triplet exciplex ^{3}(DANA$\cdots$>CO)*$_{HB}$ for the BP-DANA (RN(Me)$_2$ or R(NEt)$_2$) system. The driving force for ET is the negatively enlarged reduction potential of BP due to hydrogen bonding to the carbonyl group in ^{3}(DANA$\cdots$>CO)*.

4. ACKNOWLEGEMENT

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