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A COMPARISON OF ULTRAFAST ELECTRON TRANSFERS IN PORPHYRIN–QUINONE AND MAGNESIUM–FREE-BASE DIPORPHYRIN MOLECULES: MIMICKING PHOTOSYNTHETIC CHARGE SEPARATIONS*

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Summary

Picosecond absorption spectroscopy was used to investigate the excited state relaxations in *meso*-triphenyl(*p*-benzoquinone)porphine (P_3QP) and in solutions of *meso*-tetraphenylporphine with added amounts of *p*-benzoquinone (BQ). P_3QP has an observable S_1 state with a lifetime of less than 6 ps which decays exclusively to its lowest energy triplet T_1 and ground S_0 electronic states. The T_1 state decays in about 30 ps to yield both long-lived ($\tau > 5$ ns) electron transfer (ET) products and S_0 states. The lack of formation of a detectable ET product $^1[^- \cdot P_3QP \cdot ^+]$ from the quenching of the S_1 state of P_3QP contrasts strikingly with an earlier report of $^1[^+ \cdot \text{Mg–H}_2 \cdot ^-]$ formation from the S_1 state of Mg–H_2 in methylene dichloride (CH_2Cl_2). (Mg–H_2 is a doubly linked cofacial diporphyrin comprising magnesium porphyrin and free-base porphyrin subunits.) Here BQ quenching of the excited states of Mg–H_2 in tetrahydrofuran (THF) and CH_2Cl_2 provides spectral and kinetic evidence which confirms the prior assignment of ET in CH_2Cl_2 and $^1(\pi,\pi^*)$ formation in THF. Also, analysis of the excited state couplings in P_3QP and Mg–H_2 illustrates the important role of nuclear distortions in controlling the lifetimes of singlet biradical ET products and suggests a reason for the apparent absence of quinones as primary electron acceptors in natural photosystems.

1. Introduction

While considerable insight into the molecular properties controlling electron transfer (ET) reactions has been obtained from bimolecular systems [1 - 3], unimolecular complexes are more apt to provide data on ultrafast ETs similar

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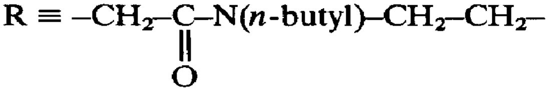
to those found in the initial charge separations in photosynthesis. Within these complexes, diffusion of the electron donor and acceptor is not required. Thus the recent syntheses of *meso*-triphenyl(*p*-benzoquinone)porphine [4] (P_3QP) and of a cofacial diporphyrin [5] $Mg–H_2$, comprising both magnesium-containing and free-base porphyrin subunits, permit detailed observation of the types of "solid state" charge separations encountered in natural photosystems. The $Mg–H_2$ and $H_2–H_2$ systems differ only in the substitution of a magnesium atom for the two central hydrogen atoms of one porphyrin ring. The $H_2–H_2$ system is composed of two (2,7,12,17-tetramethyl)-(3,13-di-*n*-octyl)porphine molecules joined at carbon atoms 8 and 18 by two covalent bridges R where



$$R \equiv -CH_2-\underset{\underset{O}{\|}}{C}-N(n\text{-butyl})-CH_2-CH_2-$$

Although quinones are important ET intermediates in both green plant and bacterial photosynthesis, they do not seem to be the first electron acceptors in any photosystem [6, 7]. Does such a situation exist of necessity or only by chance? The answer is dependent on the stability of the ET product formed by the quinone quenching of the lowest energy singlet excited state S_1 of the porphyrin or chlorophyll electron donor. Previous attempts [8, 9] to detect cation and anion photoproducts from the quenching of porphyrin and chlorophyll singlets by quinones and nitroaromatic molecules have failed. However, significant yields of ionic products are detectable when the quenching reaction proceeds from the lowest energy triplet state T_1 [10]. The explanation for this behavior [8, 11, 12] focuses on the nature of the ionic products and their relative rates of separation and back reaction. Reaction from the singlet state is presumed to form a singlet biradical in which the reverse ET within the biradical is much faster than the time for the ions to separate. Reaction from the triplet state is presumed to form a triplet biradical in which the spin-forbidden reverse ET to re-form the ground state S_0 is slow enough that the cation and anion fragments can separate.

Picosecond spectroscopy studies of P_3QP show that, while the porphyrin singlet excited state has a lifetime of less than 6 ps, no ionic photoproducts are formed from its decay. It forms triplet excited states with about 40% yield. These triplet states have lifetimes of approximately 35 ps and do yield ionic products that last for longer than 5 ns. A markedly different behavior has been reported [13] for $Mg–H_2$ in methylene chloride (CH_2Cl_2); optical spectra consonant with the formation in less than 6 ps of an ionic photoproduct $^{+}\cdot Mg–H_2\cdot^{-}$ have been presented. Also, the long-lived (about 2 ns) photoproduct observed for $Mg–H_2$ in tetrahydrofuran (THF) has been assigned as a (π,π^*) singlet excited state. These assignments of the photoproducts as ET and $^1(\pi,\pi^*)$ for $Mg–H_2$ in CH_2Cl_2 and THF respectively are based on the differences between their change-in-absorbance (ΔA) spectra. However, if they are correct, we should observe different quinone-quenching reactions for the two kinds of states. In THF the diporphyrin excited states should react similarly to the excited states of *meso*-tetraphenylporphine (TPP). In CH_2Cl_2, however, we might expect the following processes to occur:

$$\mathrm{Mg{-}H_2} \xrightarrow{h\nu} {}^1(\mathrm{Mg{-}H_2}) \tag{1}$$

$$ {}^1(\mathrm{Mg{-}H_2}) \xrightarrow{<6\ \mathrm{ps}} {}^{+\cdot}\mathrm{Mg{-}H_2}^{\cdot -} \tag{2}$$

$$ {}^{+\cdot}\mathrm{Mg{-}H_2}^{\cdot -} + \mathrm{BQ} \longrightarrow {}^{+\cdot}\mathrm{Mg{-}H_2} + \mathrm{BQ}^{\cdot -} \tag{3}$$

$$ {}^{+\cdot}\mathrm{Mg{-}H_2} + \mathrm{BQ}^{\cdot -} \longrightarrow \mathrm{Mg{-}H_2} + \mathrm{BQ} \tag{4}$$

Since reaction (4) is a bimolecular process, keeping both reactants at less than 10^{-3} M concentrations should ensure that the lifetime of the ${}^{+\cdot}$Mg–H_2 species is much greater than 10 ns. The experiments described in this paper confirm the above expectations and provide chemical evidence which substantiates the previous assignments of the excited states of Mg–H_2.

2. Experimental details

The modification of TPP to give P_3QP is described elsewhere [4]. The *p*-benzoquinone (BQ) (Aldrich) used for bimolecular quenching was purified by vacuum sublimation. Iodobenzene (C_6H_5I) (Aldrich) was redistilled prior to use and stored in the dark. CH_2Cl_2 and THF (Aldrich reagent grade) were used without further purification. The Mg–H_2 diporphyrin was synthesized as reported earlier [5].

For picosecond kinetic measurements of ΔA spectra, the samples were degassed with three freeze–pump–thaw cycles and sealed in cells of 2 mm path length. These samples were excited at 527 nm with a 6 ps laser pulse and the ΔA spectra of the resulting photoproducts were measured with an 8 ps (full width at half-maximum) white probe pulse. The entire system has been described in detail elsewhere [14].

Absorption spectra were measured on Cary 14 and Cary 17 spectrophotometers. Emission spectra and fluorescence quantum yields were measured on a Perkin–Elmer MPF-4 spectrofluorimeter equipped with a Hamamatsu R-446 multialkali photomultiplier tube and an automatic emission corrector. Fluorescence quantum yields were measured in deaerated optically dilute solutions (less than 0.08 cm^{-1}) and are relative to a yield of 0.13 for TPP in deaerated benzene [15]. Fluorescence lifetimes were measured for deaerated samples in stoppered cells of 2 mm path length. The emission was detected from the front surface of the sample with a Varian VPM-152 photomultiplier tube coupled to a 7A19 amplifier in a Tektronix 7844 oscilloscope. The response time of this system to a 6 ps laser pulse was 0.8 ± 0.2 ns. Red filters (Hoya O-56 and R-60) were used to discriminate against scattered 527 nm excitation light.

3. Results and discussion

In Table 1 the energies of the excited singlet states of P_3QP and Mg–H_2 are compared with the free energies $\Delta E_{1/2}$ required to form ${}^{-\cdot}P_3QP^{\cdot +}$ and ${}^{+\cdot}$Mg–$H_2^{\cdot -}$ from P_3QP and Mg–H_2 respectively. If the entropy changes associated with the formation of the excited singlet state are small, the free-energy change for internal

TABLE 1

Molecule	*Solvent*[a]	S_1(eV)[b]	$\Delta E_{1/2}$[c]
P_3QP	CH_2Cl_2	1.80	1.49
Mg–H_2	CH_2Cl_2	1.95	1.80[d]
Mg–H_2	THF	1.95	2.03[d]

[a] The solutions contained 0.1 M tetrabutylammonium perchlorate as an electrolyte.

[b] Energy of the lowest energy ground state absorption band about 20% along the long-wavelength edge.

[c] Estimated free-energy change for forming $^{-}\cdot P_3QP\cdot^{+}$ and $^{+}\cdot$Mg–$H_2\cdot^{-}$ from their respective ground states, calculated from the following one-electron reductions: $P_3QP\cdot^{+} \rightarrow P_3QP$; $P_3QP \rightarrow {}^{-}\cdot P_3QP$; $^{+}\cdot$Mg–$H_2 \rightarrow$ Mg–H_2; Mg–$H_2 \rightarrow$ Mg–$H_2\cdot^{-}$.

[d] Data from ref. 13.

ET from the singlet state can be estimated by subtracting its energy from $\Delta E_{1/2}$. For P_3QP and Mg–H_2 in CH_2Cl_2, ET from S_1 is favorable with the former twice as exergonic as the latter. For Mg–H_2 in THF the S_1 state is estimated to have insufficient free energy to form $^{+}\cdot$Mg–$H_2\cdot^{-}$. The following results show that the S_1 states of P_3QP and Mg–H_2 in CH_2Cl_2 are quite reactive ($\tau < 6$ ps) while that of Mg–H_2 in THF lasts for about 2 ns and has properties similar to those of the S_1 state of TPP. Thus the observed kinetic behavior is in accord with the above thermodynamic estimates of the likelihood of producing a light-driven internal ET in these compounds.

3.1. *Meso-tetraphenylporphine*

The spectral and kinetic data for TPP in CH_2Cl_2 and in CH_2Cl_2–C_6H_5I (1 : 1) are summarized in Table 2. If the radiative deactivation rate of the S_1 state of TPP is unaffected by the addition of C_6H_5I [8], the reduced fluorescence quantum yield φ_F measured in CH_2Cl_2–C_6H_5I predicts a singlet lifetime of about 0.2 ns. This agrees well with the value 0.26 ± 0.03 ns obtained from ΔA *versus* time measurements. The addition of C_6H_5I efficiently ($\varphi_T \approx 1$) populates the T_1 state from the initially formed S_1 state. Thus the $t = 0$ ps (immediately after photolysis) and the $t = 4.5$ ns ΔA spectra in CH_2Cl_2–C_6H_5I are due to the S_1 and T_1 states respectively of TPP. Knowledge of these spectra enables the S_1 and T_1 states of P_3QP to be identified.

3.2. *Triphenyl(p-benzoquinone)porphine*

The data for P_3QP in Table 2 show that the initially populated singlet excited state is observable but decays within the time of the photolysis pulse ($\tau <$ 6 ps). It is important to note that, while T_1 states are observed immediately after photolysis, ET products are not observed. The surprisingly large (about 40%) yield Y_T of triplet states is unlikely to reflect the actual quantum yield φ_T for triplet formation because the short singlet lifetime allows a P_3QP molecule to be cycled repeatedly between its ground and excited states during photolysis. This means that a relatively small triplet quantum yield ($\varphi_T < 0.05$) can produce a large triplet yield ($Y_T \approx 0.4$). The majority of the triplet states decay to the

TABLE 2

Molecular system	τ_{S_1}	φ_F[a]	Y_T (±0.1)	τ_{T_1} (ps)	Y_{ET} (±0.01)[b]	τ_{ET} (ns)
TPP in CH_2Cl_2 + 0.0 M BQ	6.3 ± 0.3 ns[c]	0.13	0.87[d]	—	—	—
TPP in CH_2Cl_2 + 0.03 M BQ	2.3 ± 0.2 ns[c, e]	0.03	0.3[f]	—	—	—
TPP in CH_2Cl_2 + 0.3 M BQ	<6, 20 ± 10 ps[g, h]	—	0.7[f]	860 ± 30	0.05	>5
TPP in CH_2Cl_2 + 1.0 M BQ	<6 ps[g]	—	0.5[f]	105 ± 15	0.05	>5
P_3QP in CH_2Cl_2	<6 ps[g]	7×10^{-4}	0.4[f]	35 ± 5	0.04	10 ± 3
TPP in C_6H_5I	260 ± 30 ps[g]	4×10^{-3}	1.0[d]	>15 ns	—	—

[a] Based on a reported value of 0.13 for φ_F for TPP in benzene [15].

[b] Based on a molar absorptivity of 1×10^4 M^{-1} cm^{-1} (±20%) for $TPP^{\cdot +}$ in the 670 nm region [16].

[c] Emission decay measurement.

[d] $\varphi_F + \varphi_T = 1$ [15, 17].

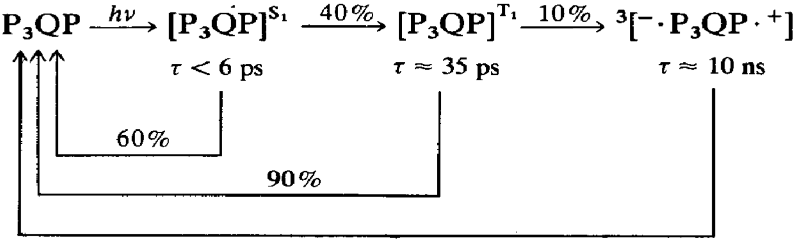
[e] A small number of the S_1 states (fewer than 10%) decayed with a lifetime of 20 ± 10 ps.

[f] Based on reported values of the molar absorptivity of the T_1 state of TPP [18].

[g] Lifetime obtained from the decay of an absorption transient.

[h] About 50% of the absorbance increase due to S_1 states decayed during photolysis.

ground state. However, about 10% produce a long-lived ($\tau \approx 10$ ns) photoproduct that has a ΔA spectrum similar to that of $TPP\cdot^+$ [16]. Since benzoquinone anions do not absorb above 500 nm [19] this ΔA spectrum is also consistent with the spectrum of ${}^3[{}^-\cdot P_3QP\cdot{}^+]$ in the 550 - 775 nm region. The results for P_3QP are summarized as follows:



$$\underset{}{P_3QP} \xrightarrow{h\nu} \underset{\tau < 6\ \text{ps}}{[P_3QP]^{S_1}} \xrightarrow{40\%} \underset{\tau \approx 35\ \text{ps}}{[P_3QP]^{T_1}} \xrightarrow{10\%} \underset{\tau \approx 10\ \text{ns}}{{}^3[{}^-\cdot P_3QP\cdot{}^+]} \qquad (5)$$

The short lifetime of the S_1 state of P_3QP can be explained on the basis of the ultrafast production of a singlet biradical ET product ${}^1[{}^-\cdot P_3QP\cdot{}^+]$. This agrees with results of previous studies in which the quenching efficiency of the excited states of porphyrins and chlorophylls by quinones and nitroaromatics has been shown to depend on the redox values of the species involved [20, 21]. The energy of the T_1 state of P_3QP is probably nearly the same as that (1.45 eV) of the T_1 state of TPP [22], given the similarities in their ground state absorbances, in the S_1 and T_1 differences and in the fluorescence spectra. This is also nearly the value of $\Delta E_{1/2}$ for forming ${}^-\cdot P_3QP\cdot{}^+$ (see Table 1). Since the T_1 and ${}^-\cdot P_3QP\cdot{}^+$ states are probably close in energy, they may be mixed. This implies that the labels ${}^1[{}^-\cdot P_3QP\cdot{}^+]$ and ${}^3[{}^-\cdot P_3QP\cdot{}^+]$ may not be a complete description of the states of the ET product. The observations that ${}^3[{}^-\cdot P_3QP\cdot{}^+]$ is quite stable ($\tau \approx 10$ ns) and that about 90% of the T_1 states decay to the ground state within a time of about 35 ps imply that the initially formed ${}^3[{}^-\cdot P_3QP\cdot{}^+]$ reacts to form the ground state of P_3QP as it vibrationally relaxes. Although this is a formally spin-forbidden ET, its rate exceeds that for vibrational relaxation of the triplet biradical. A similar reverse ET from the initially formed ${}^1[{}^-\cdot P_3QP\cdot{}^+]$ intermediate as it vibrationally relaxes is probably responsible for the production of the T_1 state.

3.3. Meso-tetraphenylporphine with added p-benzoquinone

The data for TPP in CH_2Cl_2 with 1.0 M BQ in Table 2 demonstrate that the quenching kinetics for a bimolecular system can closely approach those of the unimolecular P_3QP system. However, the data for 0.3 M BQ show that systems with large amounts of BQ may be troubled by problems of sample inhomogeneity: two S_1 state quenching times are found, less than 6 ps and 20 ± 10 ps. In both 1.0 M BQ and 0.3 M BQ the T_1 quenching process is over an order of magnitude slower than the quenching of the S_1 state. Similar kinetics are also found for BQ quenching of Mg–H_2 in THF (see below).

To understand why the ${}^1[{}^-\cdot P_3QP\cdot{}^+]$ intermediate is so short lived, it is helpful to note that (for sufficient electronic coupling) rapid ET reactions are expected if large nuclear displacements produce strong electron–vibration coupling between the potential energy surfaces of the product and reactant. The data show that the close proximity of the porphyrin and quinone subunits produces sufficient electronic coupling for rapid forward and reverse ETs. However, while a rapid forward reaction is desired, this is not true for the reverse reaction. Thus it is unfortunate (from the point of view of stabilizing the $^1[^-\cdot P_3QP\cdot{}^+]$ intermediate) that formation of $BQ\cdot^-$ is expected to produce large nuclear distortions [11, 23]. Accordingly, the crucial factor favoring a longer lifetime for $^1[^+\cdot Mg–H_2\cdot^-]$ than for $^1[^-\cdot P_3QP\cdot{}^+]$ is that the reduction of a free-base porphyrin is expected (see below) to produce much smaller nuclear distortions than is the reduction of a quinone.

3.4. *Mg–H_2 in tetrahydrofuran*

If the S_1 state of Mg–H_2 in THF is a (π,π^*) type, as suggested earlier [13], perturbation by a solvent with a heavy atom (*e.g.* C_6H_5I) should increase its intersystem crossing rate and quenching by BQ should shorten the lifetimes of both its S_1 and its T_1 states to subnanosecond times. The data in Table 3 show that in THF–C_6H_5I (1 : 1) the S_1 lifetime is reduced to 0.65 ns from about 2 ns in THF. Also, a long-lived ($\tau > 15$ ns) T_1 state is formed. When 0.25 M BQ is added to Mg–H_2 in THF, two quenching processes are observed after photolysis, with times of about 25 ps and about 470 ps. These rates are similar to the kinetic processes observed for TPP quenching by 0.3 M BQ (see Table 2). There the S_1 state of TPP was quenched in about 20 ps and its T_1 state in about 860 ps. It is worth noting that after 5 ns the ΔA spectrum between 550 and 750 nm for the BQ quenching of Mg–H_2 in THF is zero within experimental error. Thus 5 ns after photolysis the yield of any product containing a chromophore that absorbs like a porphyrin cation (about 10^4 M^{-1} cm^{-1} in the 650 nm region) is less than 2%.

TABLE 3

Mg–H_2 excited state lifetimes

Solvent	τ_{S_1}	τ_{T_1}	τ_{ET} (ps)	τ_X[a] (ns)
THF	≈2 ns[b]	—	—	—
THF–C_6H_5I (1 : 1)	650 ± 60 ps	>15 ns	—	—
THF–0.25 M BQ	<6, 25 ± 5 ps[c]	470 ± 70 ps	—	—
CH_2Cl_2	<6 ps	—	210 ± 20	$6(^{+3}_{-2})$
CH_2Cl_2–C_6H_5I (1 : 1)	<6 ps	—	200 ± 20	$12(^{+8}_{-3})$
CH_2Cl_2–0.25 M BQ	<6 ps[c]	—	92 ± 5	>15

[a] The identity of state X for Mg–H_2 in CH_2Cl_2 and CH_2Cl_2–C_6H_5I is an open question. Its ΔA spectra and lifetimes favor an assignment to a triplet biradical rather than to a (π,π^*) triplet state (see text). State X for Mg–H_2 in CH_2Cl_2 with 0.25 M BQ is $^+\cdot Mg–H_2$ (see text).

[b] The uncertainty in this lifetime is due to uncertainty in the choice of the asymptote for the decay of the S_1 state. The extreme choices of the asymptote show that τ_{S_1} is between 1.5 and 4 ns. The data are best fitted with a 2 ns decay.

[c] About 30% of the excited states of Mg–H_2 decay within 6 ps of excitation owing to static quenching by BQ (determined by comparison with the maximum ΔA observed without BQ).

3.5. Mg–H_2 in methylene dichloride

The data in Table 3 show that the perturbation of Mg–H_2 in CH_2Cl_2 by a change in solvents from CH_2Cl_2 to CH_2Cl_2–C_6H_5I (1 : 1) has no effect on the lifetime of the initially observed excited state. This state decays both to the ground state and to a long-lived state X. In CH_2Cl_2, X lives for 4 - 9 ns and in CH_2Cl_2–C_6H_5I it lives for 9 - 20 ns. Neither its lifetime nor its spectrum correspond to those of a $^3(\pi,\pi^*)$ state of a porphyrin. Rather, its spectrum suggests that it is a triplet biradical $^3[^+\cdot Mg\text{–}H_2\cdot^-]$ (see below).

On addition of 0.25 M BQ to Mg–H_2 in CH_2Cl_2, the initial photoproduct decays with a lifetime of about 90 ps and forms a much longer-lived product ($\tau > 15$ ns). This final state is unlikely to be a (π,π^*) state given its long lifetime. The simplest assignment consistent with both its Δa spectrum and its lifetime is a cation–neutral species, $^+\cdot Mg\text{–}H_2$.

Although the molar absorptivity of $^+\cdot Mg\text{–}H_2\cdot^-$ should be greater than that of $^+\cdot Mg\text{–}H_2$, this information cannot be used to identify these species unless the yield of each is known. In fact, their absorption spectra in the 550 - 750 nm region (based on the spectra [24] of the magnesium octaethylporphine cation $MgOEP\cdot^+$ and $H_2OEP\cdot^-$) are expected to appear similar. Both spectra should peak in the 660 nm region with that of $^+\cdot Mg\text{–}H_2\cdot^-$ being slightly broader on each side of this maximum. Thus it is worth noting that the ΔA spectrum of the state X produced after photolysis of Mg–H_2 in CH_2Cl_2 is similar to, but slightly broader than, the ΔA spectrum attributed to $^+\cdot Mg\text{–}H_2$. This similarity between state X and $^+\cdot Mg\text{–}H_2$ suggests that the decay of $^1[^+\cdot Mg\text{–}H_2\cdot^-]$ in CH_2Cl_2 may both reform S_0 and produce a longer-lived biradical, perhaps $^3[^+\cdot Mg\text{–}H_2\cdot^-]$.

If the molar absorptivity of $^+\cdot Mg\text{–}H_2$ is similar to that of $MgOEP\cdot^+$, a yield of about 12% can be estimated for its formation. This is about one-third of the yield expected if every dynamic quenching encounter produced separated $^+\cdot Mg\text{–}H_2$ and $BQ\cdot^-$ species (reaction (3)). (Dynamic quenching by BQ accounts for about 55% of the decay of $^1[^+\cdot Mg\text{–}H_2\cdot^-]$ present after photolysis, but 30% of the excited Mg–H_2 is quenched during photolysis. Therefore only about 38% of the Mg–H_2 sample is involved in dynamic quenching with BQ.) Thus about two-thirds of the quenching encounters short circuit $^+\cdot Mg\text{–}H_2\cdot^-$, perhaps by reacting BQ with $^+\cdot Mg\text{–}H_2\cdot^-$ near the interface of the porphyrin subunits.

The important result of the above experiments involving BQ quenching and perturbation by an external heavy atom is that quite different behavior is obtained for Mg–H_2 in THF and for Mg–H_2 in CH_2Cl_2. The excited states of Mg–H_2 in THF behave just as the S_1 and T_1 states of TPP do under the same conditions. This supports the assignment of the excited states of Mg–H_2 in THF as S_1 and T_1 (π,π^*) states. However, the initially observed photoproduct of Mg–H_2 in CH_2Cl_2 was unaffected by C_6H_5I perturbation and exhibited the kinetics and spectra expected for an $^+\cdot Mg\text{–}H_2\cdot^-$ species rather than a $^1(\pi,\pi^*)$ state.

4. Conclusion

The rapid ($\tau < 6$ ps) transformation of the singlet excited state of Mg–H_2 in CH_2Cl_2 into $^1[^+\cdot Mg\text{–}H_2\cdot^-]$ shows that the electronic coupling for forward ET is strong. Similarly the electronic coupling for the reverse ET is likely to be strong also. Why then is the reverse ET

$$^1[^+\cdot \text{Mg–H}_2\cdot^-] \xrightarrow{\tau \approx 200\ \text{ps}} \text{Mg–H}_2 + \text{X} \tag{6}$$

so much slower? The explanation for the long lifetime of $^1[^+\cdot \text{Mg–H}_2\cdot^-]$ is probably weak electron–vibration coupling between the $^1[^+\cdot \text{Mg–H}_2\cdot^-]$ and S_0 electronic states of Mg–H_2. X-ray [25] and Raman [26] studies on porphyrins and their cations and anions show that the neutral species and ions have similar bond angles, bond lengths and vibrational frequencies. Also, the large size of the diporphyrin reduces the energy requirements for solvent reorganization accompanying $^+\cdot \text{Mg–H}_2\cdot^-$ formation and decay. These considerations imply that the potential energy surface of $^+\cdot \text{Mg–H}_2\cdot^-$ will be only slightly displaced relative to those of the S_1 and S_0 states of Mg–H_2. One consequence of the small surface displacement and large free-energy change ($\Delta G \approx -1.8$ eV) for $^+\cdot \text{Mg–H}_2\cdot^-$ decay to Mg–H_2 is that this reaction is forced to be non-adiabatic. In this case the reaction rate is governed by Franck–Condon factors which determine the rate of nuclear tunneling from the upper to the lower surface. Another consequence of the small surface displacement and the large amount of free energy stored in the reaction to form $^+\cdot \text{Mg–H}_2\cdot^-$ is that the potential energy surfaces of the S_1 and $^1[^+\cdot \text{Mg–H}_2\cdot^-]$ states may cross near the minimum of the S_1 surface. Therefore the forward reaction may be nearly activationless. In this event an ultrafast ET is not surprising [27].

In summary, the Mg–H_2 diporphyrin exhibits light-driven ET kinetics and thermodynamic efficiencies comparable with those found in natural photosystems [28 - 30]. Indeed, it is a good model for the initial charge separation in photosystem II of green plants where a ligated chlorophyll-a is the postulated electron donor [31] and pheophytin-a (a metal-free chlorophyll) is the postulated acceptor [32, 33]. Also, a comparison of the light-driven ETs in P_3QP and Mg–H_2 illustrates the important role of nuclear distortions in controlling ET product lifetimes. The extreme instability of the $^1[^-\cdot P_3QP\cdot^+]$ intermediate suggests a reason for the apparent absence of quinones as primary electron acceptors despite their abundance in natural photosystems and their use as secondary ET agents [6, 7, 34].

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