intensity of the infinity spectrum (2.5% of the theoretical maximum).[11] This has a leveling effect on the influence of the nuclear spin dependence on the total exit rate for each biradical sublevel although differences as large as 30% remain. Next, the nuclear spin dependent rates are relatively slow [(3×10^4)–(3×10^6) s^{-1}]. This is the result of the poor energy match of S with the T levels. In radical pairs T_0 and S can become degenerate and spin dependent rate constants may be as large as 10^8 s^{-1}. The parameters of Figure 2 also reproduce nicely the absorption–emission features observed for **3** if a negative nuclear spin coupling constant is assumed. The origin of this multiplet effect lies in the interplay of T_0–S and $T_\pm$–S mixing and is fundamentally different from that observed in radical pairs.

Cyclooctanone shows qualitatively the same behavior, first a T_0–S spectrum followed by a predominant T_-–S pattern. However, cycloheptanone is emissive at all times signifying predominant T_-–S mixing as expected for the larger singlet–triplet splitting in a shorter biradical. Of course, the patterns observed will depend strongly on the magnitude of the reaction field because the Zeeman splitting determines the relative weight of the mixing of S with the three T levels.

In summary, we have shown here by a direct kinetic method that molecules identical in all parts of their wave function except the nuclear spin component can react with measurably different rates.

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(11) The theoretical maximum of the infinity spectrum is obtained by setting $k_{+s} \ll K_{-s} \gg k_{so}$.

Improved Energy Storage in a Two-Polyelectrolyte System

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A major goal in photochemical solar energy conversion systems involving photoinduced-electron-transfer reactions is the inhibition of the reverse-electron-transfer reaction regenerating the ground-state reactants. This may then allow useful chemical reactions to occur yielding photochemical fuels. Attempts to retard the back-electron-transfer reaction have usually been made by adding a suitable microenvironment such as micelles,[1] vesicles,[2] microemulsions,[3] charged colloids,[4] or polyelectrolytes[5-12] to the system. For example, in the presence of appropriate polyelectrolytes the yields of photoinduced-electron-transfer products may be enhanced and their rates of reverse electron transfer retarded in photochemical systems containing polypyridyl derivatives of ruthenium together with ferricyanide,[6,7] a zwitterionic viologen derivative,[8] and various polyviologens.[9,10] In this paper a new two-polyelectrolyte system is described in which isolation of the

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two final photochemical products on separate similarly charged polyelectrolytes leads to a very much greater reduction in their rate of reverse electron transfer than observed previously.

Earlier work in this laboratory has shown that reactive radical species can be very greatly stabilized when they are formed on highly charged polyelectrolytes.[13] For example, the rate of radical–radical dimerization reactions for radicals formed by hydrogen atom abstraction of quarternary ammonium cations, which usually occur close to the diffusion-controlled rate, may be inhibited by about 5 orders of magnitude when they are formed on the polyelectrolyte polybrene (repeating unit: $\{[-(CH_2)_6N-(CH_3)_2(CH_2)_3N(CH_3)_2-]^{2+}(F^-)_2\}$). This impressive reduction in rate was attributed to both the low ability of stretched polyelectrolytes to diffuse through solution and the high electrostatic repulsion of their positive charges.

Application of this result to attain stabilization of photochemical-electron-transfer products was achieved in this work by covalently bonding a photosensitizer molecule and a donor molecule to separate positive polyelectrolytes. The polyelectrolyte-linked photosensitizer I consisted of a tris(2,2'-bipyridine)ruthenium
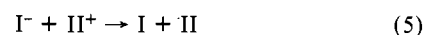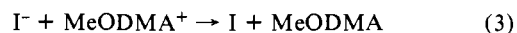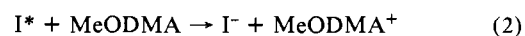

I
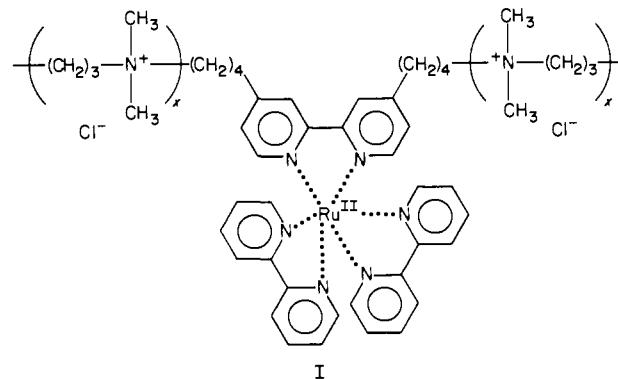
derivative linked to a poly(3,3-ionene) polyelectrolyte while the polyelectrolyte-linked donor molecule II contained an *N,N,N',*-


II
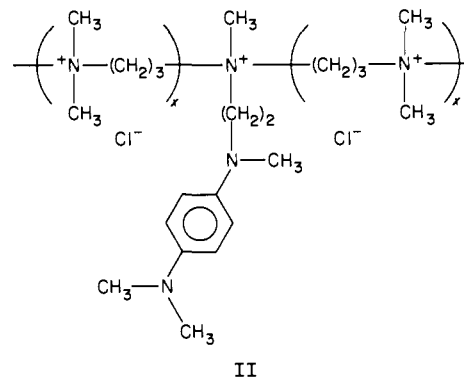
N'-tetraalkyl-*p*-phenylenediamine derivative linked to a similar polyelectrolyte. A mediator species is necessary to allow generation of the two-polyelectrolyte-linked redox products and the compound chosen was 4-methoxy-*N,N*-dimethylaniline (MeODMA) which possesses the appropriate redox potential for this electron-transfer system.[14]

Following excitation of I by light of wavelength 450 nm (eq 1) quenching of its lowest emitting excited state occurs with a

$$I \xrightarrow{h\nu} I^* \qquad (1)$$

$$I^* + MeODMA \rightarrow I^- + MeODMA^+ \qquad (2)$$

$$I^- + MeODMA^+ \rightarrow I + MeODMA \qquad (3)$$

$$MeODMA^+ + II \rightarrow MeODMA + II^+ \qquad (4)$$

$$I^- + II^+ \rightarrow I + II \qquad (5)$$

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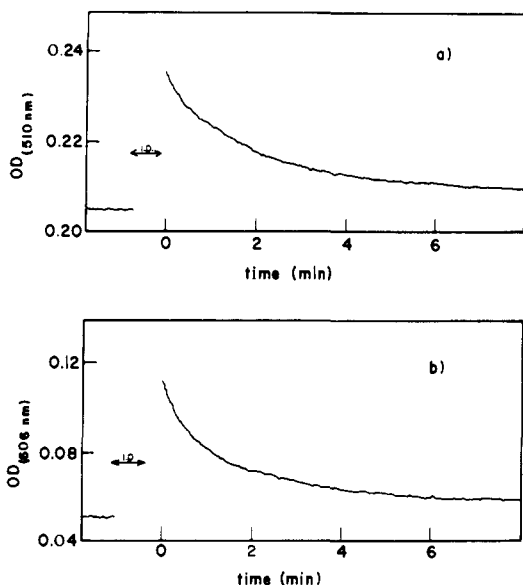
Figure 1. Decays of absorption signals of (a) I^- at 510 nm and (b) II^+ at 606 nm following irradation for 30 s at 450 nm of a solution containing 2×10^{-5} M I, 2.2×10^{-3} M MeODMA, and 1×10^{-4} M II. Path length = 4 cm; i.p. = irradiation period.

rate constant $k_2 = (1.2 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. The two initial electron-transfer products may react in a reverse-electron-transfer reaction regenerating the ground-state species, (eq 3) or in the presence of II, the MeODMA$^+$ may oxidize II to II$^+$ via reaction 4. On addition of sufficient quantity of II to scavenge MeODMA$^+$ the principle final electron-transfer products are I$^-$ and II$^+$ which would then react back via reaction 5.

The disappearance of the long-lived electron-transfer products I$^-$ and II$^+$ could be traced by observing the decays of their optical absorptions at 510 and 606 nm, respectively (see Figure 1) following 30-s irradiation of the total photochemical system in aqueous solution by light of wavelength 450 nm. The absorptions are found to decay in minutes and follow good second-order kinetics. The visible absorption spectrum of the solution before irradiation and several hours after leaving the irradiated solution in the dark were identical indicating the overall regeneration of the ground-state species. The decays are therefore attributed to reaction 5, and assuming that the electron-transfer products possess absorption spectra similar to their monomeric analogues[15] then the rate constant k_5 was estimated to be $(1.5 \pm 0.2) \times 10^4$ M^{-1} s^{-1}. This value may be compared to the known rate constant for the electron-transfer reaction between Ru(bpy)$_3$$^+$ and the cation radical of N,N,N',N'-tetramethyl-p-phenylenediamine of 5.2×10^9 M^{-1} s^{-1} in acetonitrile solution.[16] This represents a factor of inhibition of more than 5 orders of magnitude, which, even after accounting for the change in solvent, is a dramatic degree of retardation. It should be noted that in most photochemical systems studied until now factors of inhibition of the back reaction of usually about 1–2 orders of magnitude have been observed on adding microenvironments such as polyelectrolytes,[5–12] micelles,[1] vesicles,[2] microemulsions,[3] or charged colloids[4] to a photochemical system. It is also noted that irradiation of the photochemical system described for many minutes or on repeating the irradiation several times after allowing the electron-transfer products to decay back appears to lead to no change in the final absorption spectrum suggesting that very little side reaction occurs in the system which may be cycled many times. Quantitative measurements concerning the cycling of the system are currently being undertaken.

Isolating the final electron products in separate microenvironments thus appears to be very promising in allowing very high efficiencies of energy storage by the dramatic inhibition of the back-electron-transfer reaction. It is now hoped that useful chemical reactions yielding synthetic fuels will now be able to compete successfully with the impaired back reaction.

Interactions of Atomic and Molecular Iron with Methane in an Argon Matrix

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In 1979, the first direct insertion of a "ligand-free" metal atom into a carbon–hydrogen bond was reported.[1] Subsequently, it was demonstrated that the first-row late transition metals, with the exception of nickel, will undergo photoinsertion into one of the carbon–hydrogen bonds of methane to yield the methylmetal hydrides, CH$_3$MH.[2] Activation of carbon–hydrogen bonds of higher alkanes by photoexcited metal atoms has also been observed in inert gas and neat matrices.[3,4] The photochemical reaction[5] between a copper atom and a methane molecule in a neat matrix initially leads to the insertion of the metal atom into a carbon–hydrogen bond of methane followed by disproportionation of this reaction intermediate into CuCH$_3$ and H and CuH and CH$_3$. In the case of the reaction of monatomic iron or manganese with methane and hydrogen, Ozin et al.[6–8] have shown that these systems undergo photoreversible oxidative addition/reductive elimination reactions

$$M + CH_4 \underset{\lambda'}{\overset{\lambda}{\rightleftharpoons}} CH_3MH$$
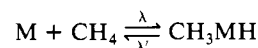
where λ = 300 (Fe) or 285 nm (Mn) and λ' = 420 (Fe) or 310 nm (Mn).

In this paper we wish to report on the first observation of a ligand-free metal methane complex in an inert gas matrix. We will further demonstrate that photoinsertion of a metal atom into the carbon–hydrogen bond of methane occurs via the formation of this hydrogen bonded complex. Diatomic iron was also found to interact with methane to form Fe$_2$(CH$_4$). Photoinsertion of the diiron into the carbon–hydrogen bond of methane was not observed.

Figure 1 depicts infrared spectra measured at different metal concentrations and obtained when iron and methane were co-

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