crepancy is not clear at present.

Ethanol addition also decreased the microviscosity. This result is explained as resulting from an increase in the micelle core's polarity and concomitant loosening of the core structure because of the interpenetration of ethanol molecules into the hydrocarbon core. A similar interpretation was put forth to explain the observed tendency for a decrease in the microviscosity with alcohol for SDS + 1-hexanol,[14] and for HDTBr + ethanol, 1-propanol, 1-butanol, or *tert*-butyl alcohol.[16]

The estimate of the microviscosity from the pyrene emissions is difficult because the pyrene forms an excimer in an intermolecular manner.[17] However, as is clear in Figures 4 and 5, the ratio I_E/I_M of pyrene appears to be a qualitative parameter of the microviscosity of the micelle core.

Conclusion

From our measurements on microviscosities under high pressure, it is concluded that DNP molecules certainly experience an environment whose structure is somewhere between that of a hydrocarbon and water. These results are interpreted to be the results of partial *penetration* of water molecules into the hydrocarbon core. The changes in the microviscosity with salt and alcohol additions may be explained as the result of *penetration* of the additives into the hydrocarbon core. Recently, Thomas et al.[18,19] estimated the polarity of hydrocarbon core from the fluorescence fine structure of pyrene. They found that the polarity of the environment of the probe was higher than that of pure hydrocarbon, from which the location of the probe was deduced to be near the micelle palisade layer between the core and the water phase. However, their results are also explainable by the water penetration mechanism.[18] We feel that the palisade positioning is conceivable if, say, one side of the pyrene molecule is stabilized by polar dispersion forces and the other side experiences hydrophobic stabilization. Decrease in the *polarity* in the presence of alcohols observed by Zana et al. can be also explained by the *penetration* mechanism of the additives into the micelle core instead of water exclusion and movement of the pyrene probe into the core.[20]

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Singlet Electronic Energy Transfer to Azoalkanes: Separation of Collisional and Long-Range Mechanisms by Steric and Solvent Viscosity Effects[†]

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Abstract: Absolute rate constants have been determined for quenching of the fluorescence of naphthalene and triphenylene by azo-*n*-butane (ANB) and azo-*tert*-butane (ATB) in five different hydrocarbon solvents of varying viscosity. The quenching process is attributed to singlet electronic energy transfer by the electron-exchange mechanism. Calculations indicate that energy transfer by the dipole–dipole (long-range) mechanism should be relatively inefficient. The observed rate constants show a linear dependence on reciprocal viscosity and are sensitive to steric effects, both indicative of a collisional mechanism for energy transfer. Rate constants for energy transfer from naphthalene to ANB are faster than those for ATB by a factor of 1.5–1.9. Rate constants for energy transfer from triphenylene exceed diffusion control in high viscosity solvents. It is suggested that a small component of the energy transfer may proceed by the dipole–dipole mechanism, and upper limits to these values are estimated.

Electronic energy transfer reactions have been demonstrated to follow at least three distinct mechanisms:[4,5] (1) "trivial" or radiative energy transfer, in which a photon is emitted by the donor and absorbed by the acceptor; (2) dipole–dipole energy transfer, in which the donor and acceptor transitions are coupled by relatively long-range Coulombic dipole–dipole interactions;[6] and (3) electron-exchange energy transfer, which requires electron-exchange interactions between the donor and acceptor molecular orbitals.[7] Triplet–triplet energy transfer can operate effectively only through the electron-exchange mechanism, while singlet–singlet energy transfer can operate through any of the three mechanisms. The electron-exchange mechanism requires close contact between the donor and acceptor, and steric effects on both triplet–triplet energy transfer[8,9,10] and singlet–singlet energy transfer[8,11-14] have been demonstrated. In this paper we present rate constants for singlet energy transfer processes which dem-

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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Table I. Fluorescence Quenching Data[a]

solvent	viscosity, cP	k_{dif}[b]	naphthalene donor k_q(ANB)	naphthalene donor k_q(ATB)	naphthalene donor steric factor[c]	triphenylene donor k_q(ANB)	triphenylene donor k_q(ATB)	triphenylene donor steric factor[c]
pentane	0.215	303 (290)	161	84	1.9 (3.0)	224	96	2.3 (6.8)
hexane	0.292	223 (210)	112	70	1.6 (2.3)	200	112	1.8 (17.6)
benzene	0.603	108 (126)	76	52	1.5 (2.2)	106	63	1.7 (5.4)
cyclohexane	0.898	73 (100)	69	41	1.7 (3.2)	105	61	1.7
cyclooctane	2.16	30 (42)	34	21	1.6 (4.2)	68	46	1.5

[a] All rate constants $\times 10^{-8}$, $M^{-1}\ s^{-1}$. [b] Calculated values from eq 3; values in parentheses are empirical values for reaction rates demonstrated to be diffusion controlled: pentane, ref 22; hexane extrapolated from pentane and heptane, ref 22 and 23; benzene, ref 23; cyclohexane and cycloctane, ref 24. [c] Steric factor defined as $k_q(\mathrm{ANB})/k_q(\mathrm{ATB})$; values in parentheses are $k_{et}(\mathrm{ANB})/k_{et}(\mathrm{ATB})$, calculated from eq 6, using the empirical values for k_{dif}.

onstrate significant steric effects and solvent viscosity effects. Based upon these effects we propose a dissection of those rate constants into components due to the electron-exchange and the dipole–dipole energy transfer mechanisms.

Experimental Section

Materials. Azo-*n*-butane and azo-*tert*-butane were prepared from the corresponding amines,[15] distilled, and determined to be >95% pure by gas chromatographic analysis. Naphthalene and triphenylene sensitizers were commercial samples, recrystallized once. Solvents were all spectrophotometric grade. Pentane was washed with H_2SO_4 and concentrated NaOH, dried over P_2O_5, and distilled.

Fluorescence Quenching. Fluorescence spectra were taken on an Aminco-Bowman spectrofluorimeter. For naphthalene, excitation was at 302 nm, and emission intensity was measured at 323 nm. For triphenylene, excitation was at 330 nm and emission intensity was measured at 370 nm. Typical sensitizer concentrations were 1×10^{-3} M, and quencher concentrations were varied from zero to 7×10^{-3} M. Samples were degassed through three freeze–pump–thaw cycles and sealed in 13 × 100-mm Pyrex culture tubes, previously cleaned and constricted. At least five different quencher concentrations were utilized to obtain each Stern–Volmer plot. Duplicate determinations indicated that the slopes were reproducible to ±10%. Quenching rate constants (k_q) were calculated from the Stern–Volmer slopes by using a literature value for the singlet lifetime of naphthalene (96 ns).[16a] The reported value for the singlet lifetime of triphenylene (36.6 ns)[16b] was confirmed under our conditions and its relative independence of solvent was verified. Measured singlet lifetimes for triphenylene were determined with a pulsed N_2 laser,[17,18] and were used in the calculation of k_q values: 35.0 ns (pentane); 33.2 ns (hexane); 32.1 ns (benzene); 36.8 ns (cyclohexane); and 33.4 ns (cyclooctane).

Calculations of Energy Transfer Parameters. The overlap integrals between the sensitizer emission spectrum and the quencher absorption spectrum were determined by the method of Berlman.[19] Emission spectra of naphthalene[16a] and triphenylene[16b] and absorption spectra of ANB and ATB[11] were traced and their intensity measured at each 100-cm^{-1} interval. The overlap integral, J_{dd} in eq 1, was approximated as the summation of the appropriate function evaluated at every 100-cm^{-1} interval, where $f(D^*)$ is the normalized fluorescence intensity of the donor

$$J_{dd} = \int \frac{f(D^*)\epsilon(A)\ d\bar{\nu}}{\bar{\nu}^4} \qquad (1)$$

and $\epsilon(A)$ is the molar decadic extinction coefficient of A. The Förster "critical distance" for 50% probability of energy transfer by the dipole–dipole mechanism was calculated from eq 2.[6,19] In eq 2, κ^2 is an orien-

$$R_0^6 = \frac{9000\kappa^2(\ln 10)Q}{128\pi^5 n^4 N} J_{dd} \qquad (2)$$

tation factor equal to $^2/_3$ for freely tumbling molecules, Q is the fluorescence quantum yield of the donor (0.23 for naphthalene[16a] and 0.08 for triphenylene[16b]), n is the index of refraction of the solvent (taken as 1.42, the average value of the five hydrocarbons used; the actual range is 1.36 for pentane to 1.50 for benzene[20]), and N is Avogadro's number.

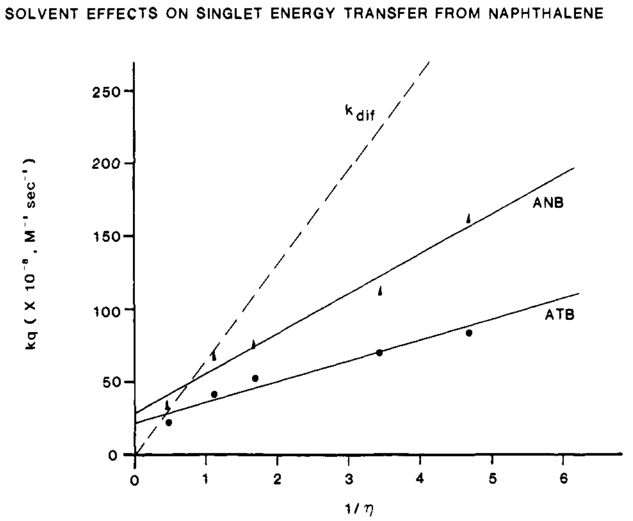

Figure 1. Rate constants for quenching of naphthalene fluorescence vs. reciprocal solvent viscosity in centipoise.

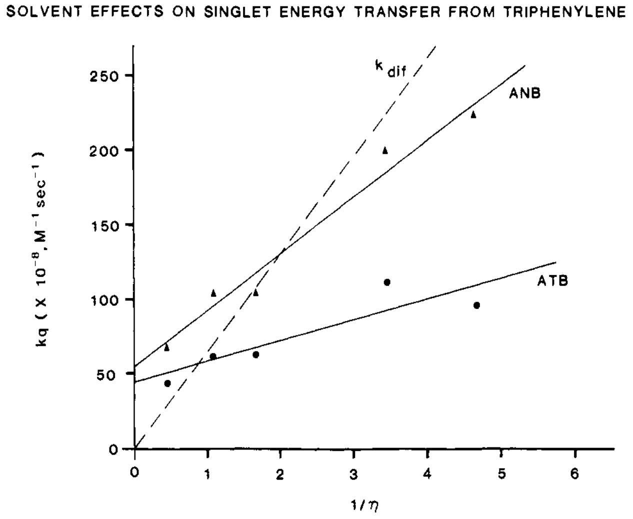

Figure 2. Rate constants for quenching of triphenylene fluorescence vs. reciprocal solvent viscosity in centipoise.

Results

Table I and Figures 1 and 2 present the rate constants for the quenching of the fluorescence of naphthalene and triphenylene by azo-1-butane (azo-*n*-butane or ANB) and azo-2-methyl-2-propane (azo-*tert*-butane or ATB). Five different hydrocarbon

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solvents were used, with viscosities varying over an order of magnitude.[20] Rate constants for a diffusion-controlled process are also shown, calculated according to the Debye equation (eq 3), in the form appropriate for large solute molecules among small solvent molecules.[21] The alternative form of the Debye equation has a denominator of 2000η, and is appropriate for small solute molecules among large solvent molecules.[21] Recent work has indicated that denominators between these two limits are often appropriate for correlation of energy transfer rate constants and that a single denominator may not correlate data for all solvents.[22] Besides the calculated values of k_{dif} from eq 3, Table I also lists maximal observed rate constants for processes considered to be diffusion controlled.[23-24]

$$k_{\mathrm{dif}} = 8RT/3000\eta \tag{3}$$

Each of the quenching rate constants are considered to be rate constants for singlet energy transfer since the relative singlet excited energy levels of naphthalene (92 kcal/mol)[25a] and triphenylene (83 kcal/mol)[25b] are substantially above the singlet excited energy levels of ANB and ATB, estimated as 70 kcal/mol from their absorption maxima. Contributions to the observed quenching caused by radiative energy transfer (reabsorption of the sensitizer fluorescence by ANB or ATB) were calculated to be negligible. Primarily because of the low extinction coefficients of the azoalkanes ($\epsilon \sim 12$ at $\lambda_{\mathrm{max}} \sim 360$ nm), less than 5% of the observed fluorescence quenching could have been caused by reabsorption. Applying the method of Marinari and Saltiel,[26] identical Stern–Volmer plots at different wavelengths were obtained, indicative of negligible radiative energy transfer.

Discussion

Steric Effects on Singlet Energy Transfer. Examples of steric hindrance to singlet–singlet electronic energy transfer have been observed with azo compounds,[8,11] ketones,[12,13] and diketones[14] as quenchers. For energy transfer to the four azobutane isomers, azo-*n*-butane (ANB) and azo-*tert*-butane (ATB) represent the extremes of least hindrance and greatest hindrance, respectively, with azoisobutane and azo-*sec*-butane giving intermediate results.[8] Only ANB and ATB were used in this study. Steric effects have been quantitated by comparing the rates for a hindered quencher and an unhindered quencher, such as $k_q(\mathrm{ANB})/k_q(\mathrm{ATB})$ in Table I. Additional values for the steric factor for this same pair have been measured by fluorescence quenching studies of acetone (acetonitrile solvent, 1.7),[8] adamantanone (acetonitrile solvent, 2.1),[8] 7,7-dimethylnorbornanone (acetonitrile solvent, 2.9),[8] and naphthalene (vapor phase, 9.5).[11] For triplet energy transfer to the same ANB/ATB pair, the steric factor ranges from approximately 3–12 for various sensitizers.[8]

In fact, the evaluation of a steric factor for energy transfer is complicated by the interplay of a variety of additional effects. The steric factor will clearly depend upon the sensitizer and its specific interactions with the quenchers; thus steric factors vary widely for different sensitizers. For singlet energy transfer in solution, the largest observed steric factor is for the sensitizer 7,7-dimethylnorbornanone (2.9),[8] and the smallest are for acetone (1.7)[8] and the planar aromatic hydrocarbons used in this study. In the absence of solvent much larger steric factors are observed, as with naphthalene in the vapor phase (9.5)[11] or the quenching of benzene fluorescence in the vapor phase by acetone and di-*tert*-butyl ketone (steric factor 4.1, vs. 1.6 in cyclohexane solution).[13] This effect is attributed to the much longer time of a solution-phase encounter compared to a gas-phase collision. Based upon the following scheme for diffusion and energy transfer,[24,27,28] the actual energy transfer rate constant (k_{et}) may not be reflected in the observed rate constant (k_q), depending upon the relative magnitudes of the rate constants for diffusion in (k_{dif}) and out ($k_{-\mathrm{d}}$) of an encounter complex.

$$\mathrm{D^* + A} \underset{k_{-\mathrm{d}}}{\overset{k_{\mathrm{dif}}}{\rightleftharpoons}} [\mathrm{D^*\ A}] \xrightarrow{k_{\mathrm{et}}} \mathrm{D + A^*}$$

$$k_q = k_{\mathrm{dif}}[k_{\mathrm{et}}/(k_{\mathrm{et}} + k_{-\mathrm{d}})] \tag{4}$$

$$k_q = \alpha k_{\mathrm{dif}} \tag{5}$$

In eq 5, α represents the fraction of encounters which lead to successful energy transfer.[24] When $k_{-\mathrm{d}}$ is small relative to k_{et}, there will be a leveling effect observed: all α values will be close to 1, and any variations in k_{et} will be obscured. In the vapor phase, where $k_{-\mathrm{d}}$ is maximal, variations in k_{et} are more clearly reflected in observed k_q values. Thus steric factors based upon relative k_q values, such as all of those quoted above, do not necessarily reflect relative energy transfer rates. Rearrangement of eq 4 for two different acceptors (a, b) in the same solvent system leads to eq 6, which provides the direct comparison of energy transfer rate constants. Using eq 6, it is clear that steric factors based upon

$$[k_{\mathrm{et}}(\mathrm{a})/k_{\mathrm{et}}(\mathrm{b})] = [k_q(\mathrm{a})/k_q(\mathrm{b})][(k_{\mathrm{dif}} - k_q(\mathrm{b}))/(k_{\mathrm{dif}} - k_q(\mathrm{a}))] \tag{6}$$

k_{et} are necessarily larger than those based upon k_q. These values are also shown in Table I. Of course, where k_q values exceed k_{dif}, this approach does not apply. In these cases, an additional mechanism for energy transfer is necessitated.

Solvent Viscosity Effects on Singlet Energy Transfer. In order to evaluate whether such diffusional effects were obscuring the actual steric effects on singlet energy transfer in solution, we undertook systematic studies to measure rate constants in solvents having different viscosities, and hence different rate constants for k_{dif} and $k_{-\mathrm{d}}$. All the solvents were hydrocarbons to minimize polar effects. This approach has been used successfully to determine the relationship between diffusion and energy transfer efficiencies.[22,24,29] Based upon the scheme described above and eq 4, there is an important criterion for obtaining useful information—that is, k_{et} and $k_{-\mathrm{d}}$ must be comparable in magnitude.[29] If $k_{\mathrm{et}} \gg k_{-\mathrm{d}}$, the leveling effect is observed, $k_q \sim k_{\mathrm{dif}}$; however, if $k_{\mathrm{et}} \ll k_{-\mathrm{d}}$, then $k_q \ll k_{\mathrm{dif}}$ and $k_q \sim k_{\mathrm{et}}(k_{\mathrm{dif}}/k_{-\mathrm{d}})$, but this function may not necessarily show any viscosity dependence. Our initial studies in low-viscosity solvents showed that for ANB and ATB, k_q was less than k_{dif} but of the same order of magnitude. Thus we considered solvents of higher viscosity to determine if the leveling effect could be observed.

As the data in Table I and Figure 1 and 2 illustrate, the observed rate constants k_q do indeed vary with solvent viscosity, but the variation fits none of the limiting cases which we originally envisioned. (1) The rate constants are not independent of solvent viscosity, as would be expected for a highly efficient singlet energy transfer entirely by a long-range (dipole–dipole) mechanism,[30,31] or for an inefficient energy transfer by a collisional (electron exchange) mechanism, where $k_{\mathrm{et}} \ll k_{-\mathrm{d}}$. (2) The rate constants are not leveled at k_{dif}, which is the observation expected for a highly efficient singlet energy transfer entirely by the electron-exchange mechanism, where $k_{\mathrm{et}} \gg k_{-\mathrm{d}}$.[30,32] (3) Even at high viscosities, the quenching rate constants for the unhindered quencher (ANB) are not leveled at the diffusion-controlled rate, as would be expected for an electron-exchange mechanism for which $k_{\mathrm{et}} < k_{-\mathrm{d}}$ at low viscosities and $k_{\mathrm{et}} > k_{-\mathrm{d}}$ at high viscosities.[24] In fact, the rate constants for ANB quenching of triphenylene are substantially

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Table II. Calculated and Experimental Data for the Dipole-Dipole Component of the Energy Transfer Rates

donor	acceptor	k_∞ ($\times 10^{-8}$, $M^{-1}\,s^{-1}$)[a]	J_{dd} ($\times 10^{17}$, $cm^3\,M^{-1}$)[b]	R_0 (Å)[e]
naphthalene	ANB	28 (12)	1.05[c]	8.4
naphthalene	ATB	22 (14)	0.83[d]	8.1
triphenylene	ANB	54 (31)	2.14	7.9
triphenylene	ATB	44 (35)	1.82	7.7

[a] Intercepts (at infinite viscosity) of the least-squares lines through the experimental data shown in Figures 1 and 2; values in parentheses are intercepts of plots vs. $\eta^{-3/4}$. [b] Calculated values of J_{dd} (eq 1). [c] Similarly calculated by Loper and Lee (ref 11) as 1.077×10^{-17}. [d] Similarly calculated by Loper and Lee (ref 11) as 0.852×10^{-17}. [e] Calculated from eq 3.

less than k_{dif} in solvents of low viscosity and somewhat higher than k_{dif} in solvents of high viscosity. We interpret this to indicate that two energy-transfer mechanisms are operative, as discussed in the following section.

Separation of the Dipole–Dipole and Electron-Exchange Mechanisms. Energy transfer by the dipole–dipole mechanism occurs through a Coulombic coupling of the donor transition ($D^* \rightarrow D$) to the acceptor transition ($A \rightarrow A^*$), specifically the electrostatic induction of a dipole in A by D*. This coupling can be accomplished through space without direct contact between D* and A. The probability of such coupling depends upon the inverse sixth power of distance (R^{-6}), the oscillator strengths of the appropriate donor and acceptor transitions, and the extent of overlap (in energy) between the two transitions (J_{dd} in eq 1).[4,6] A convenient indicator of the efficiency of energy transfer by this mechanism is the Förster "critical distance", R_0, at which the rate of energy transfer by the dipole–dipole mechanism equals the rate of deactivation of the excited state by all other natural (first-order) processes. If the dipole–dipole coupling is sufficiently weak, then this mechanism can show a dependence on diffusion—that is, the molecules must diffuse within the appropriate range of one another before the energy transfer can be effective. The diffusional dependence of the dipole–dipole mechanism has been calculated[33] and demonstrated[34,35] to be proportional to $\eta^{-3/4}$.

Energy transfer by the electron-exchange mechanism occurs through a direct exchange interaction between the excited electron of D* and the ground-state electrons of A. This interaction requires physical overlap of the donor and acceptor molecular orbitals and has an exponential distance dependence ($e^{-2R/L}$, where L is a constant). The probability of electron exchange also depends upon the energy overlap between the donor and acceptor transitions but is independent of the oscillator strengths of the two transitions.[4,7] Since this is a collisional mechanism, the dependence on diffusion is a dependence on k_{dif}, through eq 4, and k_{dif} has a viscosity dependence described by the Debye equation, that is, proportional to η^{-1}.

Singlet energy transfer to azoalkanes has been calculated to involve predominantly the electron-exchange mechanism rather than the dipole–dipole mechanism.[11,36] In particular, dipole–dipole energy transfer is made unfavorable by the extremely low oscillator strength for azoalkane absorption. Nevertheless, dipole–dipole energy transfer has been postulated to be the predominant mechanism when the donor has a very high emission oscillator strength and a good overlap integral with the azoalkane absorption.[36] For such cases, R_0 values greater than collisional distances are calculated; for example, for anthracene quenching by *cis*-azoisopropane, R_0 is calculated to be 13.6 Å, which is taken as evidence to explain the unusually high quenching rate constant in cyclohexane, $2.5 \times 10^{10}\ M^{-1}\,s^{-1}$.[36] Molecular models indicate that van der Waals contact distances for a planar aromatic hydrocarbon with ANB and ATB would be 3 and 4 Å, respectively.

Table III. Comparative Triplet and Singlet Energy Transfer Rate Constants[a,b]

donor	acceptor	k_{qt}[c]	k_{qs}[d]
naphthalene	ANB	23	76
naphthalene	ATB	6.4	52
triphenylene	ANB	32	106
triphenylene	ATB	3.0	63

[a] All rate constants $\times 10^{-8}$, $M^{-1}\,s^{-1}$. [b] In benzene solution. [c] Triplet energy transfer rate constants from ref 8. [d] Singlet energy transfer rate constants from this study.

Our results confirm that the collisional electron-exchange mechanism predominates. The sensitivity to steric hindrance is a characteristic of any collisional mechanism, and is consistent with the exponential distance dependence of the electron-exchange mechanism. The use of the viscosity dependence to confirm the electron-exchange mechanism is more problematic. The rate constants for naphthalene quenching are consistent with eq 4, but the rate constants for triphenylene quenching which exceed diffusion control lead us to believe that there is a small component of the quenching which should be attributed to the dipole–dipole (long-range) mechanism.

Calculations indicate that dipole–dipole energy transfer would be relatively inefficient. Table II lists the values for the overlap integrals (J_{dd} from eq 1) for each donor–acceptor pair and the calculated R_0 distances for dipole–dipole energy transfer. The simplest empirical method of separating the two mechanisms identifies the intercept of the reciprocal viscosity plot as an upper limit for a rate constant due to the dipole–dipole mechanism. This represents the rate constant extrapolated to infinite viscosity, or the rate constant which would remain if diffusional processes were eliminated. The intercepts of the lines from least-squares fit of the data are also shown in Table II.

Identification of the actual dipole–dipole rate constants is rendered difficult by at least two considerations: (1) the dipole–dipole mechanism has a diffusional dependence itself,[33] and (2) based on eq 4, k_q need not be a linear function of k_{dif}, in particular at high viscosities.[24] Plots of our observed k_q vs. $\eta^{-3/4}$ show linearity comparable to Figures 1 and 2 (least-squares correlation coefficients are not significantly different). The intercepts of these plots are somewhat smaller but are still nonzero; these intercepts are also shown (in parentheses) in Table II. Similar studies on singlet energy transfer[34,35] have followed linear $\eta^{-3/4}$ plots to nonzero intercepts identified as dipole–dipole energy transfer rate constants.

The efficiency of energy transfer, α in eq 5, will depend upon the relative magnitudes of k_{et} and k_{-d}, according to eq 4. Assuming that the value of k_{et} for a given donor–acceptor encounter complex does not vary much in the different hydrocarbon solvents, then the viscosity dependence of α is caused by variation in k_{-d}. Although methods have been offered for calculation of k_{-d},[22,24] comparison of two acceptors allows that term to cancel, giving eq 6. Our steric factors based on eq 6 (Table I, values in parentheses) show a reasonable constancy for naphthalene but a poor correlation for triphenylene. The k_q values which exceed k_{dif} require an additional, noncollisional mechanism. For example, subtraction of the intercept values from Table II from each k_q leads to an improved correlation.

Correlation with Triplet Energy Transfer Rates. For a triplet–triplet energy transfer, each of the individual transitions, ($D^* \rightarrow D$) and ($A \rightarrow A^*$), would be spin forbidden and only the electron-exchange mechanism can operate effectively. In general, steric factors for triplet energy transfer are substantially greater than for singlet energy transfer. In particular, even using the same donors and acceptors as in this study, significant differences are noted.[8] Table III shows the data for triplet energy transfer rate constants compared to the overall singlet energy transfer rate constants. Since the systems are as comparable as possible (same donor, acceptor, solvent), the differences do seem to be caused by the different spin multiplicities. Although both types of energy transfer should go by the same (electron-exchange) mechanism,

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the triplet energy transfer rate constants are consistently much lower. This is still true even if a small component of the singlet rate constant is removed as a contribution from dipole–dipole energy transfer. Furthermore, the steric factors are consistently larger for triplet energy transfer, where the observed ratios of k_{et} approximate the calculated value of 6.3.[8] Of the three possible reasons we postulated earlier,[8] the incorporation of an additional mechanism (dipole–dipole) into the rate constant for singlet energy transfer is seen to provide only a partial explanation. The remaining two explanations remain as viable possibilities for future investigation. (1) Triplet energy transfer may involve a spin statistical factor, which restricts the reactivity of the three triplet sublevels.[23,37] (2) For triplet energy transfer, electron-exchange coupling may require more specific interactions of the appropriate orbitals, either in terms of the extent or orientation of orbital overlap.

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Type II Photoelimination from α-Cycloalkylacetophenones and a Polystyrene-Bound Analogue[†]

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Abstract: In order to evaluate the effects of polymer binding on photoreactivity and other photochemical properties, we have synthesized α-cyclohexyl-*p*-methylacetophenone (I), α-cyclopentylacetophenone (II), and an analogue bound to insoluble polystyrene beads (P-I). All undergo type II photoelimination and are effective in energy transfer to an added quencher, *trans*-stilbene. Quantitative comparisons show that the polymer binding has little effect upon the photoreactivity as long as the polymer is in a swelling solvent, such as pentane, which allows the necessary molecular flexibility. The efficiency of energy transfer is somewhat reduced upon polymer binding.

Covalent binding of reagents and substrates to insoluble polymers has been a relatively recent development which has proved to be extremely valuable for synthetic[3-6] and mechanistic work.[7-9] In particular, photochemical studies have provided useful probes of molecular mobility and flexibility within polymeric systems.[10,11] We have begun an investigation of the possible use of polymer-bound photosensitizers in solar energy schemes. Earlier studies of polymer-bound photosensitizers have illustrated their utility; in many cases they are more advantageous than homogeneous photosensitizers.[5,12-15] Fixing the light-absorbing sensitizer on an insoluble polymer support provides the usual advantages associated with polymer-bound reagents, such as ease of separation and replacement of the different components, localization of the sensitizer, and minimization of interactions with other components of the system localized elsewhere. The particular advantage which we visualize for a polymer-bound photosensitizer is that this approach will allow the use of combinations of sensitizers. With different sensitizers fixed at different locations and unable to diffuse together, it is possible to avoid energy transfer from one sensitizer to another. In homogeneous solution, diffusional energy transfer from one sensitizer to another of lower excitation energy amounts to a degradation and wastage of part of the absorbed photon energy.

In order to function as an effective photosensitizer, the sensitizer must absorb well and transfer energy efficiently to the photoactive molecule of interest. Our first investigations, reported here, thus address the effects of polymer binding upon the spectroscopy, the photochemistry, and the energy transfer capabilities of a typical organic chromophore. We chose to study a photoreactive sensitizer because the photoreaction provides a convenient monitor for any changes in the nature of the excited state or the ability to quench that excited state. We selected the type II photoelimination reaction of aromatic ketones for several reasons: (1) It is an extremely well-characterized photoreaction, both in terms of its normal mechanism as well as the effects of different solvents and substituents.[16,17] (2) As such, it has been successfully used as a sensitive probe of microenvironments in micelles and monolayers.[18,19] (3) Excited state lifetimes are generally short but readily quenchable.[16] (4) As an elimination reaction, the photoreaction can be arranged to release a small molecule from a polymer-bound ketone (as P-I, below).

[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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