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A Case of Fully Diffusion-Controlled Exothermic Triplet Excitation Transfer[1]

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Abstract: Conventional flash kinetic spectroscopy has been used to determine rate constants ($k_{\rm obsd}$) for triplet energy transfer from indeno[2,1-*a*]indene, a rigid model of *trans*-stilbene, to azulene as a function of temperature in *n*-pentane (228–290 K), toluene (228–309 K), acetonitrile (233–308 K), and *tert*-butyl alcohol (302–342 K). In toluene the plot of $k_{\rm obsd}$ vs. T/η is linear with a slope somewhat smaller than predicted by the Debye equation for a diffusion-controlled process. In *n*-pentane the plot shows upward curvature, while in *tert*-butyl alcohol and in acetonitrile the T/η plots show downward curvature. The possibility that the downward curvature is due to deviation from a fully diffusion-controlled process is examined but rejected following a critical comparison of $k_{\rm obsd}$ with recently reported termination rate constants for coupling and disproportionation of *tert*-butyl radicals, k_t. The $k_{\rm obsd}/k_t$ ratios for the entire temperature and solvent range, 3.1–4.5, are consistent with the spin-statistical factor $\phi = {}^1/_4$, proposed as the sole deviation of k_t from a fully diffusion-controlled rate constant. Empirically based truncated microfriction factors were used to correct diffusion coefficients in the nonhydroxylic solvents, and calculated values of ϕ^{-1}, falling in the 3.5–5.0 range, were obtained that were indistinguishable from 4 within the experimental uncertainties of the measurements. It is concluded that excitation transfer is fully diffusion controlled under all conditions employed here and that, following an encounter between donor and acceptor, a probable lower limit for the rate constant of excitation transfer is $k_{\rm et} \geq 2 \times 10^{12}\ {\rm s}^{-1}$. This result is compared with observations in the literature. Satisfactory adherence to the Arrhenius equation is observed in all four solvents and activation energies are similar to activation energies for viscous flow obtained from the temperature dependence of η using the Andrade equation. Entropies and enthalpies of activation, obtained by applying transition-state theory to $k_{\rm obsd}$ and $4k_t$, obey a common isokinetic relationship, with β = 372 K as the isokinetic temperature. This isokinetic relationship is likely to apply to related diffusion-controlled reactions. Activation entropies, $\Delta S^\ddagger$, are compared to cratic entropies, ΔS_c, for the reversible formation of an encounter complex. Except for *tert*-butyl alcohol, where $\Delta S^\ddagger \simeq 0$, $\Delta S^\ddagger$ is roughly ${}^4/_3\Delta S_c$, reflecting more ordering in the transition state than in the fully formed encounter complex.

Exothermic triplet excitation transfer is often considered to occur upon every solution encounter of an excited triplet state of the donor molecule with an appropriate acceptor. This is especially true in solvents of high viscosity in which solution encounters last longer and measured triplet excitation transfer rate constants are diffusion controlled.[2] As such, their dependence on temperature, T, and viscosity, η, is expected to adhere to the Debye equation

$$k_{\rm dif} = 8RT/\alpha\eta \qquad (1)$$

which in its standard form has α = 3000 and applies to systems in which the interacting solutes are larger than the solvent molecules. Appropriate assumptions for the case of small solutes in large solvents result in a modified Debye equation with α = 2000, which appears to be in better agreement with measured rate constants of triplet excitation transfer in relatively viscous solvents.[3]

Following Hammond's study of the mechanism of benzophenone photoreduction,[5] it has become common practice to estimate lifetimes, τ_D, of triplet-state precursors to photoproducts from $k_q\tau_D$ values, obtained from the quenching effects of suitable triplet energy acceptors on reaction quantum yields, by assuming that quenching rate constants k_q are given by eq 1. However, the notion that exothermic triplet excitation transfer, in nonviscous hydrocarbon media usually employed in photochemical studies, occurs with the rate constant of diffusion together of donor and acceptor was seriously challenged by Wagner and Kochevar.[4] They noted that though a limiting rate constant of $(5 \pm 1) \times 10^9$ M^{-1} s^{-1} is obtained experimentally for a variety of donor–acceptor pairs in benzene,[6,7] this value is 2–3 times smaller than predicted by eq 1. Furthermore, estimated k_q values for quenching of valerophenone triplets by 2,5-dimethyl-2,4-hexadiene in hydrocarbon solvents (η = 0.233–3.15 cP) do not conform to eq 1 (α = 2000) except at the highest viscosities employed.[4] The discrepancy between k_q and $k_{\rm dif}$ increases as medium viscosity decreases, reaching $k_q/k_{\rm dif}$ = 0.31 in *n*-pentane (η = 0.233 cP).[4] It was reasoned that in low-viscosity media diffusion apart of donor–acceptor pairs competes with triplet excitation transfer.[4] Indirect evidence leading to the same conclusion was also obtained for the interaction of acetone triplets with each of three acceptors from a study of quantum chain processes occurring upon thermolysis of tetramethyl-1,2-dioxetane in acetonitrile.[8]

The lifetime and geometry of stilbene triplets in solution have been inferred by studying consequences of their interaction with quenchers.[1c,9] Quenching by electronic excitation transfer gives ground-state *trans*-stilbene exclusively,[10] provided that the triplet excitation energy of the acceptor is lower than ~47 kcal/mol. Azulene is an acceptor of this type and its interaction with stilbene triplets has been studied most thoroughly.[1c,9–11] The effective

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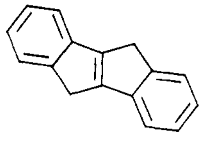
$k_q\tau_D$, obtained experimentally as a measure of this interaction, is inversely related to solvent viscosity and increases as the temperature is raised.[1c,9–11] However, k_q and/or τ_D are not simple rate constants but depend on the dynamics for twisting and decay of different stilbene triplet conformations. Electronic energy transfer is thought to occur only when stilbene triplets attain transoid conformations. In order to proceed with quantitative interpretation of such data it is necessary to know the T and η dependencies of electronic excitation transfer when the stilbene triplet is constrained to a transoid geometry. In view of the possibility that such a transfer, though exothermic by several kilocalories, might not occur upon each donor–acceptor encounter, direct measurement of its temperature and solvent dependencies was considered preferable to reliance upon the Debye equation. Results obtained for this purpose, employing indeno[2,1-*a*]indene, In, a rigid *trans*-stilbene analogue, as the donor, and azulene, Az, as the acceptor, are presented in this paper.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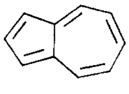
Az

Results

Rate Constants. The decay of indeno[2,1-*a*]indene triplets in solution may be written as

$$-d[^3In^*]/dt = k_1[^3In^*] + k_2[^3In^*]^2 \qquad (2)$$

where k_1 represents all first-order and pseudo-first-order decay processes depopulating triplet indeno[2,1-*a*]indene, $^3In^*$, and k_2 denotes the rate constant of bimolecular triplet–triplet annihilation of triplet states. The first-order term includes all quenching processes due to adventitious impurities as well as inherent first-order decay processes of $^3In^*$. Upon addition of triplet energy acceptor azulene in a degassed solution of small solvent volume (≲1 mL) compared to the initial cell volume (≳20 mL), the decay of $^3In^*$ obeys

$$-d[^3In^*]/dt = k_1'[^3In^*] + k_2[^3In^*]^2 \qquad (3)$$

where, assuming that the quantity of new impurities introduced is small compared to the amount of impurities already present, k_1' is given by

$$k_1' = k_1 + k_{obsd}[Az] \qquad (4)$$

where k_{obsd} is the rate constant for excitation transfer from the donor, indeno[2,1-*a*]indene, to the acceptor, azulene, and [Az] is the concentration of azulene. It follows that k_{obsd} can be calculated by determining the effective first-order decay rate constants before and after the addition of azulene

$$k_{obsd} = (k_1' - k_1)/[Az] \qquad (5)$$

Analysis of transient absorption kinetics data gives k_1 and k_1' values directly, and coefficients κ whose relation to second-order rate constants k_2 is given by

$$\kappa = k_2/\epsilon_t l \qquad (6)$$

where ϵ_t is the extinction coefficient of triplet transient absorption at the monitoring wavelength and l is the optical path length of the sample.[7,12]

Table I. Decay and Excitation Transfer Rate Constants in Toluene[a,b]

T, K	10^{-4}-(T/η), K/P	10^7-[Az], M	$10^{-3}k_1$, s^{-1}	$10^{-3}k_1'$, s^{-1}	10^{-9}-k_{obsd}, M^{-1} s^{-1}
			Run 1[c]		
228.$_2$	1.19	3.8$_7$	0.47 ± 0.01	1.46 ± 0.04	2.5$_4$
234.$_5$	1.44	3.8$_6$	0.48 ± 0.01	1.67 ± 0.06	2.9$_4$
244.$_0$	1.88	3.8$_3$	0.55 ± 0.03	1.96 ± 0.03	3.6$_7$
254.$_8$	2.47	3.8$_0$	0.56 ± 0.03	2.36 ± 0.04	4.5$_2$
264.$_0$	2.97	3.7$_7$	0.70 ± 0.01	2.72 ± 0.08	5.3$_9$
273.$_0$	3.53	3.7$_4$	0.82 ± 0.01	3.12 ± 0.05	6.3$_8$
284.$_1$	4.29	3.7$_1$	0.73 ± 0.07	3.40 ± 0.16	7.4$_6$
295.$_0$	5.14	3.6$_7$	0.84 ± 0.04	4.02 ± 0.20	9.2$_8$
304.$_4$	5.94	3.6$_3$	0.91 ± 0.09	5.17 ± 0.02	10.$_4$
			Run 2[d]		
238.$_0$	1.59	3.8$_9$	0.57 ± 0.02	1.68 ± 0.02	3.0$_0$
258.$_6$	2.67	3.8$_3$	0.71 ± 0.03	2.49 ± 0.02	4.8$_8$
264.$_2$	2.99	3.8$_1$	0.61 ± 0.03	2.71 ± 0.02	5.5$_9$
294.$_2$	5.07	3.7$_3$	0.66 ± 0.02	4.44 ± 0.09	9.7$_9$
			Run 3[e]		
234.$_7$	1.45	2.5$_4$	0.33 ± 0.01	1.13 ± 0.01	2.3$_6$
253.$_2$	2.39	2.4$_8$	0.40 ± 0.02	1.50 ± 0.03	4.3$_5$
273.$_5$	3.56	2.4$_4$	0.53 ± 0.01	2.08 ± 0.01	6.2$_9$
292.$_7$	4.95	2.3$_6$	0.75 ± 0.01	2.73 ± 0.08	8.6$_4$
309.$_2$	6.38	2.3$_5$	1.00 ± 0.04	3.78 ± 0.06	11.$_2$
			Run 4[f]		
243.$_0$	1.83	1.8$_8$	1.11 ± 0.01	1.72 ± 0.07	3.0$_6$
264.$_4$	3.00	1.8$_4$	1.55 ± 0.01	2.68 ± 0.03	5.1$_9$
282.$_8$	4.20	1.8$_1$	2.07 ± 0.02	3.22 ± 0.05	7.4$_3$
299.$_2$	5.49	1.7$_8$	2.60 ± 0.05	4.06 ± 0.01	9.5$_2$

[a] Ranges in k_1 and k_1' are either the average deviation of rate constants from duplicate oscillographic traces or the standard deviation of the fit of a single trace, whichever was larger; for viscosity values, η, see Table VIII. [b] $\kappa = 0.385T/\eta$; transient absorption monitored at 400 nm. [c] [In] = 6.4 × 10^{-5} M. [d] [In] = 6.9 × 10^{-5} M. [e] [In] = 5 × 10^{-5} M. [f] [In] = 7 × 10^{-5} M.

The azulene concentration was varied from 1.60 × 10^{-7} to 8.65 × 10^{-6} M, and the indeno[2,1-*a*]indene concentration was varied from 4.4 × 10^{-5} to 6.9 × 10^{-5} M. As a result of both the short effective lifetimes of the triplets (≲2 × 10^{-3} s) and the low indeno[2,1-*a*]indene concentrations employed, the contribution of $k_2[^3In^*]^2$ to triplet decay was minimal; consequently κ values were only poorly defined by the GENLSS computer program used in the data analysis (see Experimental Section). The best-fit κ values were assumed to be proportional to T/η as predicted by the Debye equation (eq 1) for diffusion-controlled triplet–triplet annihilation.[13] The least-squares line of a plot of κ vs. T/η was used to determine new κ values which were then inserted into the GENLSS program and held constant to obtain new k_1 and k_1' values. In those cases where identical temperatures were employed for measurements without and with added azulene, excitation transfer rate constants could be obtained by direct substitution of these k_1 and k_1' values into eq 5. However, since k_1's and k_1''s were not determined as pairs but as sets, the following procedure was deemed more appropriate and was generally employed in calculating k_{obsd}'s. The k_1 and k_1' values from each run were plotted against T/η and best-fit straight lines were drawn through the points (e.g., Figure 1). Final k_1 and k_1' values obtained from these lines were substituted into eq 5 to give the k_{obsd}'s listed in Tables I–IV. In the cases of toluene and *n*-pentane, corresponding k_1 and k_1' lines were drawn to a common intercept without significant sacrifice in the goodness of fit. For acetonitrile and *tert*-butyl alcohol the k_1' lines generally had higher intercepts than the k_1 lines, suggesting that below the experimental T/η range the k_1' lines curve downward as T/η approaches zero.

Also given in Tables I–IV are the values of $\kappa\eta/T$ in each solvent from which the κ values used in data analyses were calculated. It is important to note that owing to the small contribution of triplet–triplet annihilation as a decay process, the resulting $k_1 - k_1'$ values are not very sensitive to the choice of κ (Figure 1). Increasing or decreasing the value of κ by a factor of 2 results in a change of <10% in k_{obsd} at the largest T/η values. The sensitivity of k_{obsd} to the choice of κ diminishes as T/η is decreased.

Viscosity Measurements. Absolute viscosities, η, for acetonitrile, in the −41 to +32 °C range, were determined with *n*-pentane[15]

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(12) Herkstroeter, W. G. *Tech. Chem.* (*N.Y.*) **1972**, *1*, 521.

(13) In the case of anthracene where, due to slow unimolecular decay ($k_1 \simeq 10^2$ s^{-1}), κ's are well-defined, strictly linear dependence of κ on T/η has been established experimentally.[14]

(14) Saltiel, J.; Charlton, J. L., unpublished results.

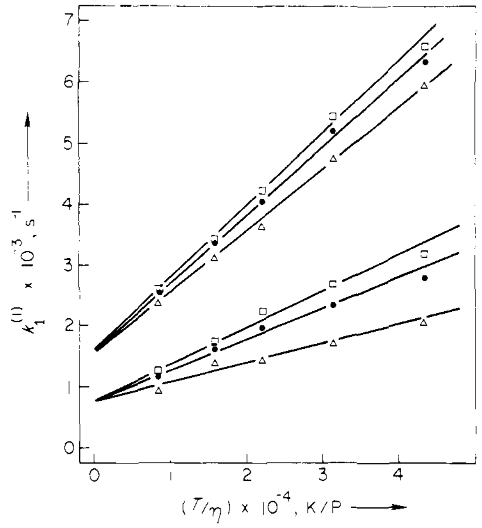

Figure 1. Typical plots of first-order rate constants for $^3In^*$ (run 2, *tert*-butyl alcohol, lower lines without and upper lines with azulene). □, ●, and △ represent best-fit $k_1^{(\prime)}$'s with $\kappa\eta/T$ = 0.212$_5$, 0.425, and 0.850, respectively.

Table II. Decay and Excitation Transfer Rate Constants in *n*-Pentane[a, b]

T, K	10^{-4}-(T/η), K/P	10^{8}-[Az], M	$10^{-3}k_1$, s^{-1}	$10^{-3}k_1'$, s^{-1}	10^{-10}-k_{obsd}, $M^{-1} s^{-1}$
			Run 1[c]		
$233._2$	5.45	8.6_5		3.16 ± 0.07	1.0_5
$233._7$	5.49		2.29 ± 0.03		
$242._7$	6.35		2.80 ± 0.01		
$243._5$	6.43	8.6_0		3.57 ± 0.06	1.2_4
$248._4$	6.93	8.5_4		3.97 ± 0.06	1.3_4
$248._6$	6.96		2.62 ± 0.01		
$258._2$	8.00	8.4_2		4.34 ± 0.07	1.6_2
$258._5$	8.03		3.04 ± 0.04		
$273._2$	9.78	8.2_4		5.08 ± 0.03	2.0_2
$273._4$	9.80		3.26 ± 0.08		
$288._2$	11.8	8.0_4		6.05 ± 0.50	2.5_0
$288._4$	11.8		3.39 ± 0.02		
			Run 2[d]		
$228._4$	5.02	7.1_1	2.20 ± 0.01	3.08 ± 0.08	0.9_1
$237._6$	5.85	7.0_4		3.32 ± 0.15	1.1_1
$238._4$	5.94		2.54 ± 0.07		
$247._6$	6.85		3.00 ± 0.03		
$248._7$	6.97	6.9_4		4.08 ± 0.05	1.3_5
$257._2$	7.88		3.52 ± 0.03		
$257._6$	7.93	6.8_7		4.18 ± 0.12	1.5_9
$267._8$	9.11		3.67 ± 0.14		
$268._0$	9.14	6.7_8		4.88 ± 0.10	1.8_9
$277._2$	10.3	6.7_1		5.50 ± 0.01	2.1_5
$278._4$	10.5		3.82 ± 0.04		
$288._2$	11.8		4.50 ± 0.03		
$290._2$	12.1	6.6_1		6.16 ± 0.18	2.6_2

[a] See footnote *a*, Table I. [b] $\kappa = 0.163T/\eta$; transient absorption monitored at 385 nm. [c] [In] = 5.9 × 10^{-5} M. [d] [In] = 6.9 × 10^{-5} M.

and toluene[15,16] as standard liquids. Absolute viscosities for acetonitrile were calculated by using the known viscosities of *n*-pentane[15] and toluene[15-17] and literature density values.[18] Reproducibility was better than ±2%. The values obtained for acetonitrile at −40.8, −20.8, −4.6, and +31.4 °C are 0.75$_2$, 0.56$_8$, 0.46$_7$, and 0.32$_8$ cP, respectively.[19]

Table III. Decay and Excitation Transfer Rate Constants in Acetonitrile[a, b]

T, K	10^{-4}-(T/η), K/P	10^{7}-[Az], M	$10^{-3}k_1$, s^{-1}	$10^{-3}k_1'$, s^{-1}	10^{-9}-k_{obsd}, $M^{-1} s^{-1}$
			Run 1[c]		
$236._3$	3.18	2.5_3	0.50 ± 0.00	2.19 ± 0.01	6.6_0
$255._2$	4.54	2.4_7	0.60 ± 0.04	2.70 ± 0.09	8.7_0
$288._0$	7.60		0.78 ± 0.03		
$290._4$	7.86	2.4_1		4.40 ± 0.15	$14._1$
$307._9$	9.91	2.3_3	1.17 ± 0.04	5.22 ± 0.10	$18._0$
			Run 2[d]		
$229._2$	2.75		0.58 ± 0.01		
$233._0$	2.98	1.9_5		2.17 ± 0.02	7.8_5
$253._7$	4.42	1.9_2	0.79 ± 0.02	2.62 ± 0.04	9.5_8
$277._4$	6.51	1.8_7	1.05 ± 0.01	3.36 ± 0.06	$12._2$
$303._3$	9.35	1.8_0		4.50 ± 0.09	$16._2$
$304._0$	9.43		1.67 ± 0.05		

[a] See footnote *a*, Table I. [b] $\kappa = 0.255T/\eta$; transient absorption monitored at 385 nm. [c] [In] = 6.4 × 10^{-5} M. [d] [In] = 4.4 × 10^{-5} M.

Table IV. Decay and Excitation Transfer Rate Constants in *tert*-Butyl Alcohol[a, b]

T, K	10^{-4}-(T/η), K/P	10^{7}-[Az], M	$10^{-3}k_1$, s^{-1}	$10^{-3}k_1'$, s^{-1}	10^{-9}-k_{obsd}, $M^{-1} s^{-1}$
			Run 1[c]		
$307._2$	1.12	3.1_0	1.29 ± 0.05	3.21 ± 0.03	6.3_5
$323._2$	2.26	3.0_6	1.89 ± 0.07	4.83 ± 0.08	9.5_4
$333._2$	3.19	2.9_5	2.02 ± 0.08	5.82 ± 0.16	$11._9$
$342._6$	4.41	2.9_2	2.84 ± 0.04	6.83 ± 0.16	$14._2$
			Run 2[c]		
$301._6$	0.853	2.3_7		2.53 ± 0.01	5.8_6
$301._8$			1.16 ± 0.01		
$313._6$	1.50	2.3_4	1.61 ± 0.01	3.32 ± 0.03	7.9_9
$322._2$	2.17	2.3_1	1.96 ± 0.05	4.03 ± 0.12	9.3_5
$331._9$	3.05	2.2_8	2.35 ± 0.01	5.22 ± 0.03	$11._9$
$342._1$	4.33	2.2_5	2.78 ± 0.04	6.34 ± 0.30	$15._1$
			Run 3[c]		
$307._8$	1.15	1.6_7	1.73 ± 0.08	2.88 ± 0.08	7.0_7
$317._3$	1.78	1.6_6	2.28 ± 0.01	3.82 ± 0.13	9.0_4
$327._2$	2.57	1.6_3	2.78 ± 0.25	4.66 ± 0.14	$11._6$
$337._7$	3.73	1.6_0	3.21 ± 0.04	5.52 ± 0.10	$14._1$

[a] See footnote *a*, Table I. [b] $\kappa = 0.425T/\eta$; transient absorption monitored at 385 nm. [c] [In] = 4.4 × 10^{-5} M.

Discussion

When transient terms can be neglected owing to long triplet donor lifetimes, $\tau_D > 10^{-6}$ s,[4] the rate constant for diffusion-controlled excitation transfer is given by

$$k_{dif} = 4\pi N\rho D/1000 \tag{7}$$

where N is Avogadro's number, ρ is the encounter distance, and D is the relative diffusion coefficient.[2] The viscosity dependence of k_{dif} and the uncertainty in α in eq 1 are, in large part, properties of the friction coefficient ζ, to which D is inversely related

$$D = kT/\zeta \tag{8}$$

where k is the Boltzmann constant.[2c] For a spherical particle of radius r the Stokes equation

$$\zeta = 6\pi\eta r(1 + 2\eta/\beta r)(1 + 3\eta/\beta r)^{-1} \tag{9}$$

where β is the coefficient of sliding friction, relates ζ to the macroscopic medium viscosity.[2c] The stick or no-slippage, β =

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[15] Rossini, F. D., et al., "American Petroleum Institute Research Project 44"; Carnegie Press: Pittsburgh, Pa., 1953; Tables 20c and 21c.

[16] Barlow, A. J.; Lamb, J.; Matheson, A. J. *Proc. R. Soc. London, Ser. A* **1965**, *292*, 322.

[17] "International Critical Tables"; McGraw-Hill: New York, 1930, Vol. VII, p 218.

[18] Reference 17, pp 29–31.

[19] Viscosities in Rossini are based on a value of 1.005 cP for water at 20 °C which has since been adjusted to 1.002 cP.[20] The resulting correction factor of 0.997 was not applied to the reported values.

[20] "Handbook of Chemistry and Physics", 53rd ed.; CRC Press: Cleveland, Ohio, 1972; p F-34.

∞, limit of eq 9 is assumed to apply for systems composed of large solutes moving among relatively small solvent molecules. This limit gives $\zeta = 6\pi\eta r$ and corresponds to the Stokes–Einstein equation for the diffusion coefficient, D_{SE}, from which the standard Debye equation, eq 1 with $\alpha = 3000$, is obtained.[2c] At the other extreme is the free-slippage, $\beta = 0$, limit which gives $\zeta = 4\pi\eta r$ and leads to the modified Debye equation, eq 1 with $\alpha = 2000$. The free-slippage limit is supposed to apply for small solutes moving among large solvent molecules when free spaces among solvent molecules are large compared to the size of solute molecules.[2c] This limit has also been applied to hydroxylic solvents even when solute and solvent molecules are similar in size.[3]

When either limiting case applies $D\eta/T$ and $k_{dif}\eta/T$ should be constants independent of viscosity. A recent review has focused on the failure of these expectations for several supposedly diffusion-controlled reactions of electronically excited molecules.[2c,21] An increase in these quantities, e.g., eq 10, is often observed which

$$k_{dif}\eta/T = a + b\eta^x \qquad (10)$$

can be rationalized in part by employing a modified D following the microfriction theory of Gierer and Wirtz.[2c,23] Several other empirical and semiempirical formulas for the calculation of D are available.[24] Experimental diffusion coefficients are usually larger than those predicted by the Stokes–Einstein relation, especially in high-molecular-weight alkanes and hydroxylic solvents.[2c] Measured D values are close to D_{SE} in nonviscous hydrocarbon solvents, and D/D_{SE} generally approaches unity as the relative size of solute to solvent molecule is increased.[2c] Rate constants for reactions considered to be diffusion controlled mirror the behavior of diffusion coefficients, their departure from values calculated from the Debye equation increasing as medium viscosity is increased or as reactant size is decreased.[2c,24,25] A recent study of exothermic triplet excitation transfer over a very wide range of temperature and viscosity (nine powers of ten) in 2-methyl-2,4-pentanediol yielded rate constants which, except at the lowest viscosities employed, are larger than those calculated from eq 1, $\alpha = 2000$, and are not adequately accounted for even by eq 10.[26]

For the relatively low viscosities commonly employed in photochemical studies eq 10 approaches eq 1, but use of D_{SE} in eq 7 usually predicts larger rate constants for exothermic triplet excitation transfer than are obtained experimentally. This deviation from theory has prompted the suggestion that donor–acceptor separation competes with triplet excitation transfer even when it is favored energetically.[2-4,8] The present work was undertaken, in part, to test the generality of this assumption.

T/η Dependence of k_{obsd}. Analysis of the excitation transfer rate constants in Tables I–IV can be based on the following sequence:

$${}^3\mathrm{In}^* + {}^1\mathrm{Az} \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} ({}^3\mathrm{In}^*{}^1\mathrm{Az}) \xrightarrow{k_{et}} ({}^1\mathrm{In}{}^3\mathrm{Az}^*) \rightarrow {}^1\mathrm{In} + {}^3\mathrm{Az}^* \qquad (11)$$

The phosphorescence spectrum of indeno[2,1-*a*]indene at 77 K gives 46.7 kcal/mol as its triplet excitation energy.[27] The triplet excitation energy of azulene, whose phosphorescence has not been observed, has been placed at 39 kcal/mol by employing it as an acceptor for a graded series of triplet energy donors.[28] In view of the high exothermicity of the transfer process and the absence of any evidence suggesting a long triplet lifetime for azulene,[28] reverse excitation transfer from azulene triplets to indeno[2,1-*a*]indene can be ignored.[2,6,29] Accordingly, the observed rate constant is given by

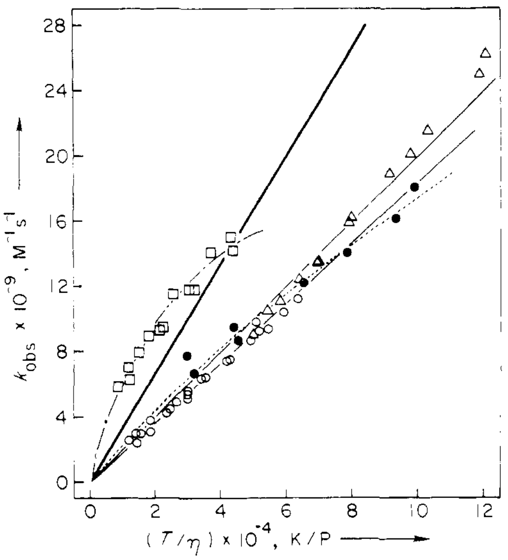

Figure 2. Dependence of k_{obsd} on T/η in *n*-pentane (△), toluene (○), acetonitrile (●), and *tert*-butyl alcohol (□). The solid line is calculated from eq 1 with $\alpha = 2 \times 10^3$.

Table V. Parameters for Eq 1 and 12

solvent	ξ,[a] M	$10^{-3}\alpha$	$10^{-12}k_{et}$, s^{-1}	p[e]
n-pentane	8.7	3.2[b]		1.00
		3[c]	$\geqslant 2$	0.89–0.96
toluene	9.4	3.7[b]		1.00
		3[c]	0.40	0.76–0.94
acetonitrile	19.1	2.9[d]	1.4	0.78–0.92
		3[c]	1.6	0.80–0.93
tert-butyl alcohol	10.6	0.83[d]	0.26[d]	0.41–0.78

[a] Solvent molarity at 293 K (see text). [b] Assuming $k_{obsd} = k_{dif}$ and eq 1. [c] Assuming Stokes–Einstein limit of eq 1 and using eq 13. [d] From eq 13. [e] Range of p (see eq 12).

$$k_{obsd} = \frac{k_{dif}k_{et}}{k_{-dif} + k_{et}} = \frac{k_{dif}k_{et}}{\xi k_{dif} + k_{et}} = pk_{dif} \qquad (12)$$

where $k_{dif}/k_{-dif} = \xi^{-1}$ and p is the efficiency of excitation transfer following a donor–acceptor encounter. Assuming that the enthalpy change for formation of the encounter pair in eq 11 is zero, ξ can be estimated from the entropy change (cratic), ΔS_c, for bringing two solutes together. For a net change of one solute molecule $\Delta S_c = -R \ln [\mathrm{M}]$, where [M] is the molarity of the solvent; thus, $\xi = [\mathrm{M}]$.[30] For the limiting case of $k_{et} >> \xi k_{dif}$, $k_{obsd} = k_{dif}$ and, according to eq 1, a plot of k_{obsd} against T/η should be linear with a zero intercept. Downward curvature in such a plot would be expected when ξk_{dif} is not negligible. This condition is most likely to obtain in the least viscous solvents.[4,5] It is striking, therefore, that the plot of k_{obsd} vs. T/η for *n*-pentane shows upward curvature, while for toluene it is linear with a zero intercept (Figure 2). In *n*-pentane $k_{obsd}\eta/T = (2.00 \pm 0.08) \times 10^5$ M^{-1} s^{-1} K^{-1} P over the T/η range employed, giving $\alpha = 3.3_3 \times 10^3$ in eq 1, in good agreement with the Stokes–Einstein limit of the Debye equation, $\alpha = 3 \times 10^3$. In toluene $k_{obsd}\eta/T = (1.82 \pm 0.08) \times 10^5$ M^{-1} s^{-1} K^{-1} P, which results in a slightly larger value of $\alpha = 3.6_5 \times 10^3$. The acetonitrile points exhibit more scatter but are generally in the same region as the *n*-pentane and toluene points (Figure 2). However, some downward curvature is suggested when the line is forced through the origin.

Standing apart are the *tert*-butyl alcohol points. Here, downward curvature is observed although the rate constants are, with a single exception, larger than predicted even by the α =

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(21) There are exceptions: e.g., for the self-diffusion of water $D\eta/T$ is constant in the 278–328 K range.[22]

(22) Wang, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 510, 4181.

(23) Gierer, A.; Wirtz, K. *Z. Naturforsch., A* **1953**, *8*, 532.

(24) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130 and references cited.

(25) See Ware (Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455) for an early demonstration.

(26) Dainton, F. S.; Henry, M. S.; Pilling, M. J.; Spencer, P. C. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 257.

(27) Saltiel, J.; Khalil, G.-E.; Schanze, K. *Chem. Phys. Lett.* **1980**, *70*, 233.

(28) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161 and references cited therein.

(29) Nordin, S.; Strong, R. L. *Chem. Phys. Lett.* **1968**, *2*, 429.

(30) Gurney, R. W. "Ionic Processes in Solution"; McGraw-Hill: New York, 1953.

2×10^3 limit of eq 1 (Figure 2). Assuming, for the moment, that the curvature is due to inefficiency in the excitation transfer process, substitution of eq 1 into eq 12 and rearrangement gives

$$k_{\mathrm{obsd}}\eta/T = (8R/\alpha)(1 - k_{\mathrm{obsd}}\xi/k_{\mathrm{et}}) \qquad (13)$$

from which the parameters $\alpha = 8.3 \times 10^2$ and $k_{\mathrm{et}} = 2.6 \times 10^{11}$ s^{-1} can be obtained by plotting $k_{\mathrm{obsd}}\eta/T$ vs. k_{obsd} and using the value of ξ given in Table V. The small change in ξ with temperature (<10%) was neglected because it does not influence the magnitude of these parameters. The acetonitrile data and eq 13 give $\alpha = 2.9 \times 10^3$ and $k_{\mathrm{et}} = 1.4 \times 10^{12}$ s^{-1}.

It seems significant that the α values for the three nonhydroxylic solvents are close to 3000, the Stokes–Einstein limit of the Debye equation. As indicated above, this limit is expected to apply best when solute molecular radii, r, are larger than solvent molecular radii, r_{L}.[2c] Since in our systems $r/r_{\mathrm{L}} > 1$, diffusion coefficients in fair agreement with the Stokes–Einstein values are likely.[2c] The small deviations of the experimental α's (Table V) from 3000 could reflect (1) deficiencies in the simple theory,[24] including the clearly incorrect assumption of spherical solute and solvent molecules,[31] and/or (2) departures from completely efficient excitation transfer in the encounter cage, i.e., $p < 1$ in eq 12. If the latter possibility were correct and α were equal to 3000 for purely diffusion-controlled transfer, satisfactory fits to the experimental data would result with $k_{\mathrm{et}} = 1.6 \times 10^{12}$ s^{-1} in acetonitrile and $k_{\mathrm{et}} \geq 4.0 \times 10^{11}$ s^{-1} in toluene (Table V). The absence of any hint of downward curvature in *n*-pentane suggests $k_{\mathrm{et}} \geq 2 \times 10^{12}$ s^{-1} in that solvent. However, it must then be concluded that, due primarily to a fivefold larger value of k_{et}, excitation transfer is more nearly diffusion controlled in *n*-pentane than in toluene though the former is the less viscous solvent.

In the case of *tert*-butyl alcohol the deviation of α from either theoretical limit of eq 9 is unmistakable and shows that Osborne and Porter's conclusion that $\alpha = 2000$ in hydroxylic solvents[3] is not generally valid. The much lower value of $\alpha = 8.3 \times 10^2$ must reflect high diffusion coefficients for solutes in alcohols,[2c,3,25,34] which are not accounted for by eq 8 and 9.[24]

Relationship to Earlier Work. The necessity of treating alcohol solvents separately when considering rate constants for diffusion-controlled reactions was recognized by Ware and Novros in their study of anthracene fluorescence quenching by carbon tetrabromide.[34] Satisfactory agreement between observed and calculated rate constants was obtained by assuming that in the expression $D = CT/\eta$ the value of the constant C is 2.2 times larger in isobutyl alcohol than in heptane, benzene, or acetonitrile.[34] The correction factor was based on higher measured diffusion coefficients of bromoform in several alcohols.[35]

Comparison of the η dependence of exothermic triplet excitation transfer rate constants in hydrocarbon and alcohol solvents was attempted in the pioneering study of Wagner and Kochevar.[4] Stern–Volmer constants, $k_{\mathrm{obsd}}\tau_{\mathrm{D}}$, for the quenching of valerophenone photoelimination by 2,5-dimethyl-2,4-hexadiene were converted to triplet excitation transfer rate constants by taking $k_{\mathrm{obsd}} = 5 \times 10^9$ M^{-1} s^{-1} in benzene[6,7] and then assuming that τ_{D} is solvent independent.[4] The k_{obsd}'s obtained in hydrocarbon solvents were treated by using eq 1, $\alpha = 2000$, and eq 12 by assuming further that the ratio k_{et}/ξ is solvent independent.[4] Comparison of the quenching of acetophenone formation from excited γ-phenylbutyrophenone by *cis*-1,3-pentadiene in dilute pentane and neat *cis*-1,3-pentadiene solutions gives a limiting value of $k_{\mathrm{et}} \geq 9 \times 10^{10}$ s^{-1} from which $\xi \geq 5$ was calculated. It was concluded that only in the more viscous cycloalkane solvents $p \rightarrow 1$ and $k_{\mathrm{obsd}} \simeq k_{\mathrm{dif}}$.[4] Better comparison with the present results is achieved by treating the k_{obsd} values in ref 4 and by using eq 13 without preselecting α but assuming that ξ is entirely determined by the cratic entropy for bringing donor and acceptor together in each solvent;[30] i.e., ξ = solvent molarity.[36] The scatter of the points in the resulting plot of $k_{\mathrm{obsd}}\eta/T$ vs. $k_{\mathrm{obsd}}\xi$ (Figure 3) strongly suggests that a single value of α will not account for the data. This was recognized specifically for the case of *n*-hexadecane in the previous treatment by plotting the *n*-hexadecane point using $\eta/2$ instead of η.[4,37] The line drawn in Figure 3 with $\alpha = 3000$ and $k_{\mathrm{et}} = 2.0 \times 10^{11}$ s^{-1} accommodates nicely all *n*-alkane points except for *n*-hexadecane unless the latter is plotted using $\eta/2$ as suggested.[4] The cycloalkane and benzene points also deviate significantly from the line. The deviation of the benzene point is more distressing since all other k_{obsd} values are based on the donor lifetime inferred for that solvent; it suggests a somewhat longer (~25%) τ_{D} in saturated hydrocarbons than in benzene. Since r/r_{L} varies with solvent, different values of α in these systems would not be surprising.[2c,24] Nonetheless, the behavior in Figure 3 is consistent with Wagner and Kochevar's conclusion that excitation transfer from valerophenone triplets to 2,5-dimethyl-2,4-hexadiene is not fully diffusion controlled in most, if not all, the hydrocarbon solvents employed.

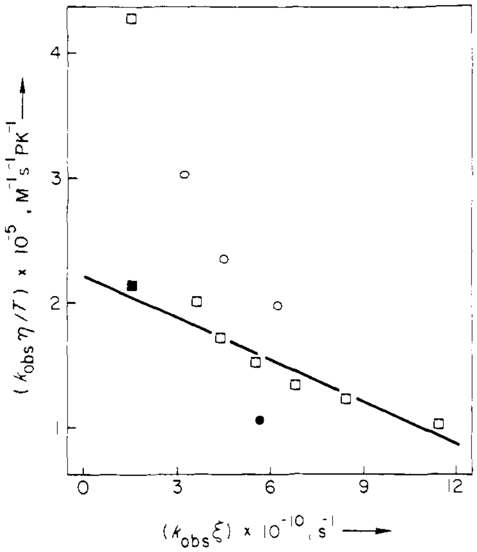

Figure 3. Treatment of the Wagner–Kochevar data using eq 13: □ and ○ are used for alkanes and cycloalkanes, respectively, ● is used for benzene, and ■ is the *n*-hexadecane point plotted using $\eta/2$ (see text).

In contrast to the results in Figure 3, $k_{\mathrm{obsd}}\tau_{\mathrm{D}}$ is almost linearly dependent on η^{-1} for three tertiary alcohols, suggesting that excitation transfer is fully diffusion controlled in these solvents.[4] The slope of that line gives $\alpha = 8.9 \times 10^2$ for tertiary alcohols if the estimated value of τ_{D} in benzene is employed. Here, too, direct measurement of τ_{D} is necessary in order to determine whether the agreement between this α value and that obtained in the present study for *tert*-butyl alcohol is more than coincidental.

The efficiency of exothermic triplet excitation was considered more recently by Takemura et al.[38] Extending experiments by Steel and co-workers,[39] they determined the temperature dependencies of acetophenone phosphorescence and of Stern–Volmer constants for the quenching of this phosphorescence by 1,4-dibromonaphthalene in isopentane, isooctane, and carbon tetrachloride solutions. Unfortunately, the interpretation of these data was based on the assumption that in the absence of added 1,4-dibromonaphthalene the lifetime of acetophenone triplets is determined by diffusion-controlled impurity quenching occurring with the activation energy of viscous flow, ΔE_{η}. Actually, the

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(31) For a recent extension of the theory to rotational diffusion coefficients of prolate and oblate ellipsoids and its experimental application see ref 32 and 33, respectively.

(32) Hu, C.; Zwanzig, R. *J. Chem. Phys.* **1974**, *60*, 4354.

(33) Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Am. Chem. Soc.* **1974**, *96*, 6840.

(34) Ware, W. R.; Novros, J. S. *J. Phys. Chem.* **1966**, *70*, 3246.

(35) Stearn, A. E.; Irish, E. M.; Eyring, H. *J. Phys. Chem.* **1940**, *44*, 981.

(36) Solvent molarities ranging from 3.4 for *n*-hexadecane to 11.3 for benzene (average ξ = 7.2 M) were calculated from densities at 293 K. See: Lange, N. A., Ed., "Handbook of Chemistry", 9th ed.; Handbook Publishers: Sandusky, Ohio, 1956.

(37) Gorrell, J. H., Jr.; Dubois, J. T. *Trans. Faraday Soc.* **1967**, *63*, 347.

(38) Takemura, T.; Aikawa, M.; Baba, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2476.

(39) Clark, W. D. K.; Litt, A. D.; Steel, C. *Chem. Commun.* **1969**, 1087.

Table VI. Ratios of Excitation Transfer and Radical Termination Rate Constants

solvent	T range,[a] K	k_{obsd}/k_t
n-pentane	233–278	3.6–3.9
toluene	248–306	3.4–3.1
acetonitrile	266–306	4.5 ± 0.1
tert-butyl alcohol	300–340	3.8–3.2

[a] For acetonitrile and *tert*-butyl alcohol overlapping temperature ranges are given; for *n*-pentane and toluene k_{obsd}'s are compared with k_t's for *n*-heptane and benzene, respectively, and the temperature ranges are chosen so that T/η in the solvent pairs overlap.

lifetime of acetophenone triplets in aliphatic hydrocarbon solvents is determined by the rate constant of hydrogen atom abstraction, the activation energy for which, ΔE_a, depends on the type of hydrogen which is being abstracted (primary, secondary, or tertiary) and sometimes on the specific hydrocarbon.[40] For example, in the case of isooctane[41] $\Delta E_a = 4.1$ kcal/mol[40] would impose a much steeper τ_D temperature dependence than predicted on the basis of $\Delta E_\eta = 2.1$ kcal/mol.[38,40] Since, contrary to what was assumed, $k_{dif}\tau_D$ will not be temperature independent, the conclusions in ref 38 may not be reliable.

A most revealing comparison with the present work is provided by Schuh and Fischer's extensive investigation of *tert*-butyl radical self-termination rate constants, k_t.[24] Plots of k_t vs. T/η for 12 solvents generate a family of at least seven lines with slopes increasing with solvent molecular weight (*n*-heptane through *n*-hexadecane) and solvent association (tertiary alcohols). The range of slopes is larger than predicted by the stick and slip limits of the Stokes equation (eq 9), indicating that neither can be applied generally for calculation of diffusion coefficients. Following an evaluation of nine empirical or semiempirical methods for the calculation of D, it was concluded that for nonassociating solvents the formula of Spernol and Wirtz[42] gives reliable results, whereas for alcohols the formula of Gainer and Metzner[43] is best.[24] It was noted that these two methods modify the Stokes–Einstein relationship for D by accounting for (1) the molecular sizes of solute and solvent and (2) the effects of different solute–solvent and solvent–solvent interactions.[24] Semiempirical formulas for D suggest the necessity of such modifications.[24] Substitution of calculated D's into eq 7, with $\rho = 2r_{t\text{-Bu}}$, gives encounter rate constants in adequate agreement with measured k_t's throughout the solvent and temperature ranges, provided that a spin-statistical factor $\phi = {}^1/_4$ is included. It was concluded that only singlet radical pairs self-terminate and that, within the uncertainties in experimental k_t's and calculated D's, they do so on every encounter; i.e., $k_t = {}^1/_4 k_{dif}$.[24]

The variation of k_{obsd} with T/η (Figure 2) parallels closely that found for k_t; in particular, both k_t and k_{obsd} plots show pronounced downward curvature in *tert*-butyl alcohol. Ratios of k_{obsd}/k_t for identical or related solvents are shown in Table VI. For *tert*-butyl alcohol and acetonitrile, ratios were calculated directly from the data. For toluene and *n*-pentane k_{obsd} were related to k_t's for benzene and *n*-heptane, respectively, by adjusting the k_t's for small differences in T/η. Plots of k_{obsd} vs. k_t are shown in Figure 4. The range of k_{obsd}/k_t ratios, 3.1–4.5, is remarkably close to the inverse of the proposed statistical factor, $\phi^{-1} = 4$. Since D and ρ in eq 7 are solute dependent, k_{obsd}/k_t ratios do not give ϕ^{-1} directly. However, inclusion of solute-specific correction factors for the three nonhydroxylic solvents, using the method of Spernol and Wirtz,[42] does not alter the result significantly (see Table VII and Appendix). The ϕ^{-1} range, 3.5–5.0, obtained using truncated microfriction factors is, within experimental uncertainty, indistinguishable from 4, the proposed spin-statistical value. This result represents persuasive evidence that both triplet excitation transfer from ^{3}In* to ^{1}Az and t-Bu self-termination are fully diffusion-controlled reactions, or nearly so, in all solvents employed.

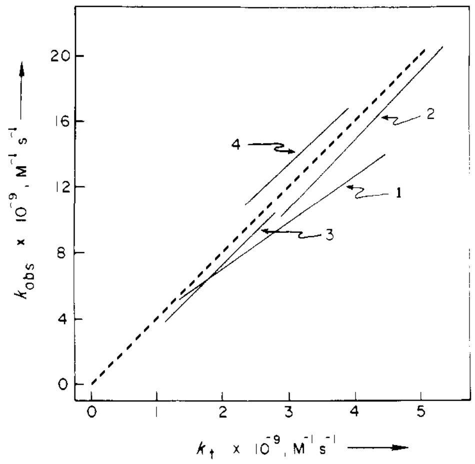

Figure 4. Plot of k_{obsd} vs. k_t: lines 1–4 show measurements in *tert*-butyl alcohol, *n*-pentane/*n*-heptane, toluene/benzene, and acetonitrile, respectively. The dashed line is drawn with 0 intercept and slope 4.

Schuh and Fischer concluded that the approach of Spernol and Wirtz underestimates D's for t-Bu in *tert*-butyl alcohol by at least a factor of 3. This is not surprising since D_{exptl} for alcohols were not included in the Spernol and Wirtz data set. On the other hand, the method of Gainer and Metzner,[43] which was recommended for alcohol solvents, does not apply to In and Az because it was developed for liquid solutes. Nonetheless, the fact that k_{obsd}/k_t is very close to 4 in this solvent also (Table VI) suggests that most, if not all, of the curvature in the k_{obsd} vs. T/η plot is reflective of the behavior of D's in *tert*-butyl alcohol and not of larger deviation from the diffusion-controlled limit. In other words, it seems very likely that both k_{et} and the range of p obtained from eq 13 for *tert*-butyl alcohol (Table V) are grossly underestimated.

Concerning k_{et}. Since the curvature in the T/η plot for *tert*-butyl alcohol (Figure 2) seems to be inherent in D, the value $k_{et} = 2.6 \times 10^{11}$ s^{-1} (Table V) establishes the lower limit of k_{et} for the ^{3}In*/^{1}Az system. This limit is shifted to a higher value of $k_{et} \geq 2 \times 10^{12}$ s^{-1} when one considers the *n*-pentane plot for which, if anything, the curvature is upward. Since k_{et} is not expected to be particularly sensitive to solvent, the limit $k_{et} \geq 2 \times 10^{12}$ s^{-1} probably applies to all solvents in this study. It is important to recognize that this conclusion is based on the assumption that an exciplex with significant bonding interaction does not lie in the excitation transfer path.[2d] If formation of the (^{3}In*^{1}Az) encounter pair were accompanied by a favorable enthalpy change, smaller ξ values in eq 13 would result and lower k_{et} values would be consistent with k_{obsd}. With $\Delta H = 0$ for the encounter, the lower limit for k_{et} inferred above is larger than most previous estimates involving organic molecules in solution.

Triplet excitation transfer is considered to involve an electron-exchange interaction which requires sufficiently close approach between donor and acceptor to allow overlap between electronic orbitals. An expression for the rate of excitation transfer by this mechanism between atoms in a crystal lattice was derived by Dexter.[44] It relates k_{et} (eq 14) to an exchange interaction

$$k_{et} = (2\pi/\hbar)Z^2 \int_0^\infty F_D(\nu)\epsilon_A(\nu)\,d\nu \tag{14}$$

energy term Z^2, and the overlap integral of the normalized singlet–triplet emission and absorption spectra of donor and acceptor, respectively. Because the vibrational factors occurring in the triplet transfer and the triplet spectra are not always the same, the overlap integral has been modified recently to include only the normalized components of the spectra which arise from direct first-order spin–orbit coupling.[45] Z^2 is expressed approximately as $K \exp(-2R/L)$, where K is related to specific orbital interactions, R is

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[40] Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953 and references cited.

[41] There is some ambiguity here since ref 39, but not ref 38, specifies that the name is applied to 2,2,4-trimethylpentane.

[42] Spernol, A.; Wirtz, K. *Z. Naturforsch., A* **1953**, *8*, 522.

[43] Gainer, J. L.; Metzner, A. B. *AIChE-I. Chem. Symp. Ser.* **1965**, *No. 6*, 74.

[44] Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

[45] Davidovich, M. A.; Knox, R. S. *Chem. Phys. Lett.* **1979**, *68*, 391.

Table VII. Microfriction and Spin-Statistical Factors

		full[b]				truncated[c]			
solvent (r_L, Å)[a]	T, K	f_t^{In}	f_t^{Az}	$f_t^{t\text{-Bu}}$	ϕ^{-1} [d]	f_t^{In}	f_t^{Az}	$f_t^{t\text{-Bu}}$	ϕ^{-1} [d]
n-pentane (3.2_3)	233	1.04	0.76	0.50	6.2	0.64	0.58	0.54	4.0
	278	1.05	0.78	0.51	6.8				4.3
toluene (3.1_5)	228	0.99	0.71	0.45	6.2	0.66	0.59	0.55	3.8
	309	0.98	0.73	0.45	5.7				3.5
						0.74[e]	0.64[e]	0.59[e]	3.6–3.9
acetonitrile (2.4_9)	233	1.14	0.82	0.50	8.5	0.79	0.70	0.66	5.0
	308	1.18	0.87	0.53	8.3				5.0

[a] Radii (eq 27): r_L from d_4^{20}; $r = 3.9_2$, 3.3_6, 3.08 Å for In, Az, and *t*-Bu, respectively, assuming $d = 1.0$ for In (e.g., *trans*-stilbene $d_3^{125} = 0.970$) and Az (e.g., 1-methylnaphthalene, $d_4^{14} = 1.025$) and using isobutane as a model for *t*-Bu. [b] mp (°C): −129.7, −95, −44.9, −145, 208, and 99 for *n*-pentane, toluene, acetonitrile, *t*-Bu (isobutane), In, and Az, respectively. bp (°C) in the same order: 36.1, 110.6, 81.6, −12.2, ~334 (isomer 1-phenylnaphthalene as model), 270 dec. [c] f_t(trunc) assumed temperature independent. [d] From eq 26. [e] Interpolated from plot of D_{exp} in toluene vs. r/r_L.[42]

the distance between donor and acceptor, and L is the mean effective Bohr radius of excited donor and ground-state acceptor atoms.[44] The exponential factor is due to the assumption that beyond some minimum R value electron density falls exponentially with distance from each atom.[44,46] Dexter estimated $k_{et} = 10^{10}$–10^{11} s^{-1} when donor and acceptor atoms occupy nearest like-lattice sites in a crystal such as NaCl.[44]

Dexter's exchange mechanism has been applied to triplet excitation transfer between organic molecules in crystals and in glassy and fluid solutions.[2,46] In rigid organic glasses where a fixed random distribution of donor and acceptor molecules can be assumed, incorporation of the exponential distance dependence in k_{et} predicts nonexponential decay of triplet donor in the presence of acceptor.[47] This prediction has been confirmed for two donor–acceptor systems: benzophenone–naphthalene in diethyl ether–methylcyclohexane[48] and carbazole–naphthalene in ethanol–diethyl ether[49] (both studies at 77 K). From the resulting empirical parameters L and R_0, the donor–acceptor distance for which the transfer rate constant, $k_{et}(R_0)$, is equal to the donor decay rate constant, $1/\tau_D$, in the absence of acceptor, extrapolated limiting values of k_{et}^0 can be calculated using $k_{et}(R) = k_{et}^0 \exp(-2R/L)$.[49] For donor benzophenone[48] $1/\tau_D = 2.22 \times 10^2$ s^{-1}, $L = 1.10$ Å, and $R_0 = 13.7$ Å give $k_{et}^0 = 1.5 \times 10^{13}$ s^{-1}, whereas for donor carbazole[49] $1/\tau_D = 0.123$ s^{-1}, $L = 1.07$ Å, and $R_0 = 15.1$ Å give $k_{et}^0 = 2.2 \times 10^{11}$ s^{-1} (ref 49 gives $k_{et}^0 = 1.8 \times 10^{11}$ s^{-1}). It should be stressed that the significance of these extrapolated k_{et}^0's is not clear because the exponential distance dependence is expected to break down at short R's. The limitation becomes obvious when one attempts to calculate k_{et} for nearest-neighbor donor–acceptor pairs using the exponential relationship with R equal to the sum of the van der Waals radii of donor and acceptor. When $R = 4$ Å is used for the carbazole–naphthalene system, an absurdly low value of $k_{et} = 1.0 \times 10^8$ s^{-1} is obtained.[49] Interestingly, both studies give $L = 1.1$ Å as the average Bohr radius of donor and acceptor. This value[50] has been suggested to represent interaction between 2p orbitals in which, at the transfer distances involved, electrons experience an effective nuclear charge of +1.[49] If this is correct, the effect on L of delocalization over extensive π systems would be negligible at such distances.[52]

Other experimental estimates of k_{et} stem from investigations of systems in which the transfer is intramolecular[54–56] and from direct transient absorption measurements in the picosecond time scale.[57] These studies, including Wagner and Kochevar's, have in common a benzoyl moiety as the n, π^* triplet donor and a naphthalene or olefin moiety as the acceptor. The largest estimated k_{et} value for intramolecular excitation transfer is 7.2×10^{10} s^{-1}.[55] This result is in excellent agreement with direct transient absorption measurements employing triplet benzophenone as donor and the acceptors *cis*- and *trans*-1,3-pentadienes and α-methylnaphthalene as solvents.[57] Considering only static excitation transfer, k_{et} values of (0.8–1.7) × 10^{11}, (0.7–1.2) × 10^{11}, and (0.4–0.7) × 10^{11} s^{-1} were obtained for the three acceptors, respectively. The differences in k_{et} were attributed to the relative size of the overlap integrals in eq 14.[57]

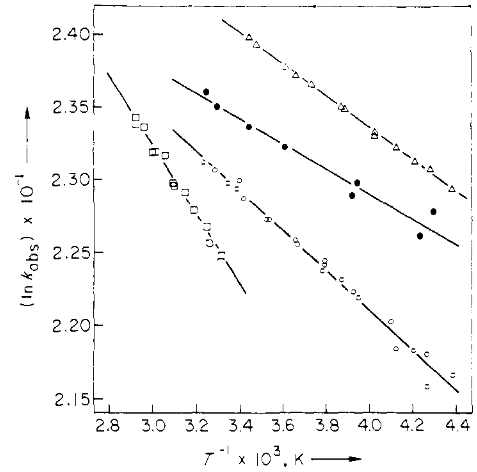

Figure 5. Arrhenius treatment of k_{obsd}: △, ●, ○, and □ represent measurements in *n*-pentane, acetonitrile, toluene, and *tert*-butyl alcohol, respectively.

Empirical Z values for eq 14 have been estimated from rate constants of singlet excitation transfer from aromatic donors to azoalkanes.[58] Substitution of optimum values of the exchange integral, ~3 × 10^4 cm, and Z, ~100 cm^{-1}, from Table II of ref 58 into eq 14 predicts $k_{et} \simeq 3 \times 10^{12}$ s^{-1} for allowed exchange-induced excitation transfer.[59] Our conclusion that $k_{et} \geq 2 \times 10^{12}$ s^{-1} for ^{3}In*/Az is consistent with this value. Why, then, are k_{et} values for excitation transfer from n, π^* benzoyl triplets to π, π^* acceptors at least an order of magnitude smaller? An analysis of energy transfer rate constants from triplet acetone to different

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Table VIII. Andrade and Arrhenius Parameters[a]

solvent[b]	T, K	$\log A_\eta$	$E^\ddagger{}_\eta$	$\log A_{\text{obsd}}$	$E^\ddagger{}_{\text{obsd}}$	$\log 4A_t$	$E^\ddagger{}_t$
n-pentane	233–273	−3.63	1.35	12.07 ± 0.05	2.19 ± 0.05		
	273–303	−3.67	1.40				
toluene	203–253	−4.33	2.73	11.98 ± 0.2	2.72 ± 0.10		
	253–323	−3.85	2.17				
acetonitrile	232–305	−3.66	1.63	11.45 ± 0.2	1.7_2 ± 0.3	11.63 ± 0.05	2.0_3 ± 0.2
		(−3.62)	(1.58)				
tert-butyl alcohol	302–321	−7.45	8.27				
		(−7.42)	(8.14)	13.17 ± 0.1	4.7_0 ± 0.04	13.71 ± 0.1	5.3_6 ± 0.2
	321–347	−6.43	6.77				
		(−6.43)	(6.69)				

[a] A_η in poise; A_{obsd} and A_t in M^{-1} s^{-1}, E's in kcal/mol. [b] Viscosity sources: *n*-pentane, ref 15; toluene, $T \geqslant 248$ K, ref 15; acetonitrile, see text and ref 20: *tert*-butyl alcohol, ref 17, p 216. Andrade parameters in parentheses are from ref 24.

acceptors has led to the attractive proposal that the strong localization of excitation in n, π^* states leads to inefficient triplet excitation transfer.[60] In every case, (n, π^*)–(n, π^*) is much slower than (n, π^*)–(π,π^*) energy transfer. In the present case, the strong delocalization of donor and acceptor π, π^* states probably reduces the sensitivity of the efficiency of the process to the mutual orientation of donor and acceptor in the solvent cage and accounts for the larger k_{et} value.[61]

Activation Parameters. The above comparison between k_{obsd} for triplet excitation transfer and k_t for radical termination supports the view that both processes are fully diffusion controlled. Accordingly, eq 12 reduces to $k_{\text{obsd}} = k_{\text{dif}}$ and it is proper to examine the Arrhenius behavior of k_{obsd} directly. As shown in Figure 5 the adherence of k_{obsd} to the Arrhenius equation

$$\ln k_{\text{obsd}} = \ln A_{\text{obsd}} - E^\ddagger{}_{\text{obsd}}/RT \qquad (15)$$

is satisfactory in all four solvents ($r^2 \geq 0.96$). The temperature dependence of viscosity may be expressed approximately in terms of the Andrade equation

$$\ln \eta = \ln A_\eta + E^\ddagger{}_\eta/RT \qquad (16)$$

where η is the absolute viscosity in poise, $E^\ddagger{}_\eta$ is the activation energy for viscous flow, and A_η is a constant for a given solvent. Least-squares fit parameters for the Arrhenius and Andrade equations are given in Table VIII. In the cases where significant systematic deviations of the viscosity from Andrade behavior are noted, low- and high-temperature regions were treated separately, resulting in ranges of $E^\ddagger{}_\eta$ and A_η. For acetonitrile and *tert*-butyl alcohol Andrade parameters obtained from the results of Schuh and Fischer are also given.[24] It should be noted that since there is compensation between $\log A_\eta$ and $E^\ddagger{}_\eta$, there is excellent agreement between the two studies in the case of acetonitrile. For *tert*-butyl alcohol the viscosities of Schuh and Fischer are consistently ~14% lower than literature values,[17] possibly reflecting the presence of 3% by volume di-*tert*-butyl ketone in the Schuh and Fischer solvents.

In contrast to *tert*-butyl alcohol where $E^\ddagger{}_\eta > E^\ddagger{}_{\text{obsd}} \simeq E^\ddagger{}_t$, activation energies for the reactions in the nonhydroxylic solvents are either very close to or somewhat smaller than $E^\ddagger{}_\eta$. Treatment of the rate constants in terms of transition-state theory

$$\ln (k_{\text{obsd}}/T) = \ln (k/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT \qquad (17)$$

allows calculation of entropies and enthalpies of activation for solute–solute encounters in each solvent. Analogous parameters can be calculated from the *tert*-butyl radical termination rate constants by replacing k_{obsd} by $4k_t$ in eq 17, where the factor of 4 adjusts k_t to k_{dif} by canceling the spin-statistical factor (Table IX). Figure 6 demonstrates the existence of a common isokinetic relationship[62]

$$\delta\Delta H^\ddagger = \beta\delta\Delta S^\ddagger \qquad (18)$$

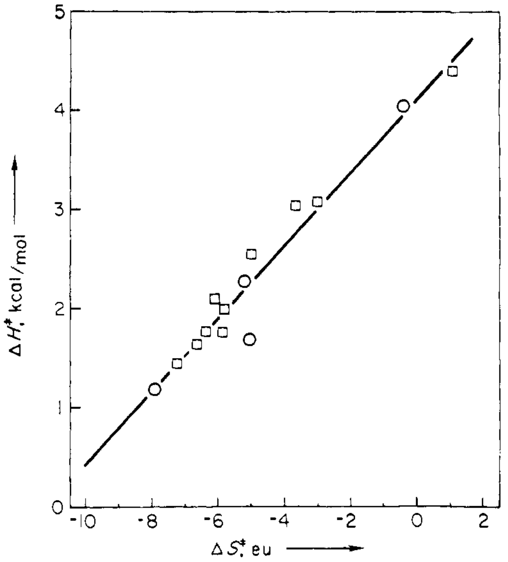

Figure 6. Isokinetic plot of the parameters in Table IX: ○, this work; □, data from ref 24 (see text).

Table IX. Thermodynamic Parameters[a]

solvent	$\Delta H^\ddagger{}_{\text{obsd}}$	$\Delta S^\ddagger{}_{\text{obsd}}$	$\Delta H^\ddagger{}_t{}^b$	$\Delta S^\ddagger{}_t{}^b$	$\Delta S_c{}^c$
n-pentane	1.68	−5.03			−4.30
n-heptane			1.77	−5.85	−3.81
n-octane			1.65	−6.63	−3.63
n-decane			2.00	−5.79	−3.25
n-dodecane			2.11	−6.10	−2.95
n-tetradecane			2.55	−4.98	−2.68
n-hexadecane			3.05	−3.65	−2.44
benzene			1.79	−6.37	−4.82
toluene	2.28	−5.20			−4.45
acetonitrile	1.19	−7.91	1.45	−7.24	−5.86
tert-butyl alcohol	4.06	−0.404	4.41[d]	1.06[d]	−4.69

[a] ΔH's in kcal/mol., ΔS's in cal/deg. [b] From rate constants in Tables II and III in ref 24. [c] Calculated from $\Delta S_c = -R \ln [M]$, where $[M]$ is the solvent molarity at 20 °C. [d] Data in the 299–356 K range.

between the activation entropies and enthalpies for triplet excitation transfer and radical termination. The presence of this relationship is consistent with the conclusion that the two processes have a common mechanism: diffusion through the solvent, leading to a fully effective encounter, is in each case the activated process. The slope of the line gives β = 372 K as the isokinetic temperature. A marked tendency for reaction series in which the solvent is the variable to have β values in the 300–400 K range has been noted.[62]

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Since both reactions were studied at lower temperatures than β, changes in $\Delta H^\ddagger$ are controlling in the behavior of observed rate constants.

Also shown in Table IX are cratic entropy changes, ΔS_c, for a reversible encounter in each solvent.[30] Excepting *tert*-butyl alcohol, ΔS_c is roughly $^3/_4\Delta S^\ddagger$. In other words, the activation entropy for an encounter of hydrocarbon solutes in nonhydroxylic solvents reflects more ordering in the solvent than is required for the fully formed encounter complex. In the case of *tert*-butyl alcohol the activation entropy is close to zero, suggesting that the cratic entropy change is a poor measure of the entropy change for the formation of an encounter complex between two nonhydroxylic solutes in a hydroxylic solvent. It appears that in such a system a major contributing factor to the entropy change is disruption of ordering in the solvent, the latter being less ordered for isolated solutes.

Experimental Section

Materials. ***n*-Pentane** (Fisher, Spectroanalyzed) was chromatographed through a silver nitrate/alumina column[63] immediately before use. ***n*-Pentane** (Phillips commercial grade) was washed three times with fuming sulfuric acid, three times with saturated aqueous sodium bicarbonate, and three times with distilled water, then distilled crudely, passed through silica gel, and fractionally distilled using a 13-mm o.d. × 4-ft vacuum-jacketed column filled with Helipac packing (Podbielniac Corp.). **Toluene** (Fisher, reagent grade) was washed with portions of concentrated sulfuric acid until no discoloration of the acid layer occurred, then twice with saturated aqueous sodium carbonate, and repeatedly with distilled water, dried over anhydrous calcium chloride, and distilled over phosphorus pentoxide. **Acetonitrile** (Malinckrodt, reagent grade) was purified as described by O'Donnell, Ayres, and Mann.[64] ***tert*-Butyl alcohol** (Matheson Coleman and Bell, reagent grade) was distilled over potassium metal. **Azulene** (Baker, reagent grade) was sublimed twice, mp 99.0–100.5 °C. The preparation of **indeno[2,1-*a*]indene** using a significantly improved modification of the available synthesis,[65–68] which raises the overall yield from 1 to 25%, is described below. **α,β-Diphenylsuccinic acid**: Ethyl phenylacetate (80 g) was added to sodium methoxide (27 g) in dry tetrahydrofuran at −80 °C rapidly with stirring, followed immediately by a cooled solution of iodine (64.5 g in 300 mL of dried tetrahydrofuran) over a 10-min period (exothermic reaction). The solution was stirred 5-min at room temperature, and 100 mL of 5% aqueous sodium bisulfite was added. The mixture was refluxed 4 h with 100 g of potassium hydroxide in 1.5 L of water. Distillation of most of the tetrahydrofuran followed by acidification with concentrated hydrochloric acid and cooling precipitated α,β-diphenylsuccinic acid. The crystals were filtered, washed with a little warm water and dried under vacuum; yield: 41.5 g, 82%. **9,10-Dioxosuccindane**: Powdered diphenylsuccinic acid (40 g) was added with vigorous stirring to 3.5 L of polyphosphoric acid (85% P_2O_5) at 100 °C in a 5-L flask equipped with a mechanical stirrer, and the temperature was raised to 125–130 °C. Product formation was monitored by quenching 1-mL aliquots on crushed ice, extracting with chloroform, drying the solution with magnesium sulfate, and observing the carbonyl band at 1710 cm^{-1} and anhydride absorptions at 1775 and 1850 cm^{-1}. After 21 h the temperature was raised to 150 °C for 2 h. The solution at 80 °C was poured into 6 L of ice–water, stirred for 2 h, and filtered. The solid was agitated with 1 L of hot 5% sodium bicarbonate, filtered, and dried under vacuum. The powder was sublimed at 150 °C under high vacuum and the sublimate was mixed with 5 g of charcoal powder and slowly resublimed to give 9,10-dioxosuccindane: 77% yield (26.1 g); ^{1}H NMR δ 4.33 (s, 2 H), 7.1–8.0 (m, 8 H). **9,12-Dichlorodiphensuccindadiene**: 9,10-Dioxosuccindane (11.4 g) and phosphorus pentachloride (21.0 g) were weighed into a round-bottom flask and covered with 150 mL of chloroform dried by passage through alumina. The flask, fitted with a reflux condenser and gas outlet, was warmed in a water bath. At about 50 °C vigorous reaction necessitated cooling in an ice bath. After spontaneous reflux stopped, the solution was refluxed 30 min and the resulting solution was further dried by warming to 80 °C in vacuo for 2 h. This crude material consists of 9,12-dichlorodiphensuccindadiene and some 9,9,12,12-tetrachlorodiphensuccindane. **Indeno[2,1-*a*]indene** (diphensuccindene-10): The crude product from the previous reaction was dissolved in 250 mL of boiling acetic acid and zinc dust (12 g) was added slowly in 2-g portions, the initially vigorous reaction being allowed to subside between additions. Stirring and heating with 5 g of additional zinc dust was continued for 1 h. The suspension was filtered hot, the solid was washed with boiling acetic acid (3 × 50 mL), and the combined filtrates were evaporated to dryness. The solid was sublimed at 150 and 110 °C under vacuum, recrystallized from ethyl acetate after treatment with 0.5 g of charcoal, and resublimed to yield 3.3 g (32% yield, based on 9,10-dioxosuccindane): mp 207.1–208.2 °C (lit. mp 208 °C[66]); ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 4 H), 6.7–7.6 (m, 8 H). The sample was purified further by recrystallization, five times, from ethyl acetate followed by zone refining (86 passes) before use in kinetic studies. The final material was a white crystalline substance.

Flash Kinetic Analysis. A Northern-Precision kinetic flash photolysis apparatus was employed. Triple-jacketed cells similar to that described by Jackson and Livingston[69] were used which allow temperature control by circulation of a transparent liquid (methanol or methanol–water) through an outer jacket. A Haake constant-temperature circulator and an external cooling circuit were employed. No temperature difference for the circulating liquid at the entrance and exit of the outer cell jacket was detected. Solution temperatures are considered accurate to better than ±0.5 °C. At least 20 min was allowed for equilibration. All solutions were rigorously degassed using 6–8 freeze–pump–thaw cycles to stick vacuum. A polaroid camera was used to photograph the oscilloscope display of the triplet–triplet absorption curve. Following measurements of the decay characteristics of ^{3}In*, an azulene solution (0.5–1.0 mL) was admitted into the cell (average volume 20 mL) via a break seal and a fritted-disk filter, which prevented glass fragments from entering the cell, and the decay of ^{3}In* photographed again. The photographs were enlarged by projection and values of the signal as a function of time were measured with a ruler. Transient decays were primarily first order, but second-order components were exactly accounted for by using the integrated expression for mixed first- and second-order triplet decay[70] in conjunction with GENLSS, a general least-squares computer program.[71]

Viscosity Measurements. An Ubbelohde viscometer, Cannon no. 1, A 738, courtesy of Professor L. Mandelkern, was employed. The thoroughly cleaned and dried viscometer was charged with liquid (the same as in the flash kinetic experiments) and allowed to equilibrate thermally for at least 20 min in a thermostated bath prior to flow-time measurements. Three time measurements were made with each solvent. The bath temperature was monitored with the same calibrated iron–constantan thermocouple used in the flash kinetic experiments.

Absorption Spectra. Infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer and NMR spectra were obtained with a Varian A-60 spectrometer.

Appendix

Microfriction Factors. We consider, here, only the Spernol and Wirtz[42] approach to calculation of D's because it was preferred[24] for three of the four solvents used and because needed parameters are either available or can readily be approximated. For a large number of solute–solvent systems (excluding alcohols), Spernol and Wirtz showed that empirical microfriction factors for translation, f_t, obtained from ratios of D_{SE} to experimental diffusion coefficients D_{exptl}

$$f_t = kT/6\pi\eta r D_{exptl} = D_{SE}/D_{exptl} \qquad (19)$$

are, on the average, dependent on r/r_L according to[42]

$$f_t = 0.16 + 0.4r/r_L \qquad (20)$$

A theoretical expression, derived to correct the stick limit of the Stokes equation, eq 9 with $\beta = \infty$, for the finite thickness of solvent layers, predicts f_t' values in satisfactory agreement with empirical

$$f_t' = [(1.5r_L/r) + 1/(1 + r_L/r)]^{-1} \qquad (21)$$

eq 20.[23] Because systematic solvent- and solute-specific deviations remained between experimental f_t's (eq 19) and f_t's predicted by eq 20, an attempt was made to improve the fit of eq 20 by relating these deviations to reduced solvent and solute temperatures, T_{rL}

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and T_r, respectively.[42] Reduced temperatures are defined by

$$T_{r(L)} = (T - T_{mp(L)})/(T_{bp(L)} - T_{mp(L)}) \quad (22)$$

where T is the experimental temperature and $T_{mp(L)}$ and $T_{bp(L)}$ are the melting point and boiling point of the solute or solvent, respectively. Resulting correction terms were assumed to be additive and to be related to specific interactions between solvent–solvent and solvent–solute molecules.[42] The full expression for f_t is accordingly given by

$$f_t = (0.16 + 0.4r/r_L)(0.9 + 0.4T_{rL} - 0.25T_r) \quad (23)$$

Use of the reduced temperature term in eq 23 in an attempt to extract solvent- and solute-independent f_t's improves the fit to eq 20 marginally, reducing the average deviation from ~12 to ~8%.

Use of eq 20 to predict f_t's has been advocated by Alwattar, Lumb, and Birks.[2c] D's are then calculated from

$$D = kT/f_t\zeta = kT/\zeta_\mu \quad (24)$$

which is eq 8 with Stokes' friction coefficient ζ replaced by the microfriction coefficient ζ_μ. It was proposed further that the stick limit of eq 9, $\zeta = 6\pi\eta r$, be replaced by the slip limit, $\zeta = 4\pi\eta r$, when $r/r_L < 1$.[2c] Though this suggestion may have merit, it neglects the fact that eq 20 is based on f_t's calculated by using the stick limit for ζ, eq 19, regardless of the r/r_L value, $0.72 \le r/r_L \le 1.84$.[42] Thus, the excellent agreement between experimental D's for several solutes in *n*-hexadecane, $0.60 \le r/r_L \le 0.80$, and D's predicted by eq 24 with $\zeta = 4\pi\eta r$[2c] is probably fortuitous.

Schuh and Fischer estimated full microfriction factors, f_t(full), and truncated microfriction factors, f_t(trunc), for the *tert*-butyl radical, *t*-Bu, with eq 23 and 20, respectively, using isobutane or *n*-butane as models for *t*-Bu. D's were calculated from eq 24 with $\zeta = 6\pi\eta r$ for all r/r_L consistent with the definition of the empirical f_t's. The contribution of the reduced temperature term in eq 23 increases as the molecular weight of the solvent is increased. This is evident in the series of *n*-alkane solvents, C_7 to C_{16}, where f_t(trunc)/f_t(full) increases from 1.2 to 1.7. For the higher molecular weight alkanes only f_t(full) gives D's in good agreement with values calculated by other empirical methods. Consequently, f_t(full) was used generally to calculate *t*-Bu encounter rate constants.[24] It should be noted that because the reduced temperature term in eq 19 was developed from diffusion coefficients for relatively low boiling point solutes and solvents (e.g., *n*-octane was the longest chain *n*-alkane solvent represented in the data set) to compensate marginally for rather small deviations from eq 20 (≤25%), its use with higher molecular weight solvents or solutes represents a risky extrapolation.

Assuming that k_{obsd} and k_t are fully diffusion controlled, but including the spin-statistical factor, ϕ, in k_t, gives

$$\frac{k_{obsd}}{k_t} = \left(\frac{1}{\phi}\right)\left(\frac{\rho_{et}}{\rho_t}\right)\left(\frac{D_{et}}{D_t}\right) \quad (25)$$

where ρ_{et} and ρ_t are encounter radii for triplet excitation transfer and radical self-termination, respectively, and D_{et} and D_t are the corresponding diffusion coefficients, eq 7. Assuming ρ's and D's equal to the sums of the molecular radii and the diffusion coefficients of the reactants, respectively, and solving eq 19, 24, and 25 for ϕ^{-1} gives

$$\phi^{-1} = \left(\frac{k_{obsd}}{k_t}\right)\left(\frac{4r_{Az}r_{In}}{r_{Az} + r_{In}}\right)\left(\frac{f_t^{Az}f_t^{In}}{f_t^{t\text{-Bu}}(f_t^{Az}r_{Az} + f_t^{In}r_{In})}\right) \quad (26)$$

where $f_t^{t\text{-Bu}}$, f_t^{Az}, and f_t^{In} are translational microfriction coefficients for *t*-Bu, Az, and In, respectively, and the molecular radii, r_x, of the reactants are obtained from the molar volumes, V_x in cm^3, using

$$r_x = (3000V_x\chi/4\pi N)^{1/3} \quad (27)$$

where $\chi = 0.74$ is the space-filling factor for closest packed spheres.[2c,24,42]

Calculated f_t(trunc), f_t(full), and corresponding ϕ^{-1} values are listed in Table VII. Molecular radii were not adjusted for temperature changes. Since r_x is proportional to $d^{-1/3}$, it is not very sensitive to density changes. In any case, such changes should cancel out in r/r_L ratios, and f_t(trunc) (eq 20) should not vary significantly with temperature. Similarly, f_t(full) is nearly temperature independent, owing to complementary changes in solvent and solute reduced temperature terms in eq 23. The large values of ϕ^{-1}, 5.7–8.3, obtained using f_t(full) are not considered trustworthy. As pointed out above, reduced temperature corrections for high molecular weight solvent or solute molecules fall well outside the empirical $\Delta f_t/f_t$ range which served as basis for eq 19, e.g., for In $0.44 \le \Delta f_t/f_t \le 0.61$. On the other hand, the ϕ^{-1} range, 3.5–5.0, obtained using f_t(trunc) is remarkably close to 4, the proposed spin-statistical value. As a further test of the conclusion that f_t(trunc) in eq 26 is much more likely to give correct predictions, f_t values were intrapolated directly from a plot of D_{exptl} in toluene vs. r/r_L.[42] The microfriction factors obtained (Table VII) are almost identical with f_t's calculated with only the solvent reduced temperature correction in eq 23. The predicted range of ϕ^{-1}, 3.6–3.9, is well within experimental error of 4, and in excellent agreement with the range predicted using f_t(trunc).

Carbanion Photochemistry. 3. Electron Transfer and Radical-Anion Control in the Photochemistry of Triphenylmethyl Anion[1]

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Abstract: On the basis of concentration and competition studies, the photomethylation of triphenylmethyl anion in dimethyl sulfoxide is shown to involve the reaction of methyl radical with triphenylmethyl anion to yield the radical anions of 1,1,1-triphenylethane and 3-(diphenylmethylene)-6-methyl-1,4-cyclohexadiene. However, there are no chain-carrying steps as there are for typical $S_{RN}1$ reactions. The intervention of radical anions produces the unconventional product of para alkylation, but the reaction is dominated by the bond strength of the newly formed bond as indexed by pK_a.

Recently we observed the facile photomethylation of resonance stabilized carbanions in dimethyl sulfoxide.[2] Our subsequent work in this area has led us to the conviction that the overwhelming reaction pathway is electron transfer, despite some rather for-

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