Benzophenone and 2,2-Dimethyl-1,3-dioxole (1b). The reaction mixture contained only one product according to chromatographic analyses. Even benzpinacole was not formed as shown by comparison with an authentic sample.[33b] After filtration of a solution in *n*-hexane/ethyl acetate (98/2) over silica gel (Woelm, Si 100/200) the product was further purified by means of HPLC and identified as 3,3-dimethyl-7,7-diphenyl-2,4,6-trioxabicyclo[3.2.0]heptane, **7b**. ^{1}H NMR (CCl_4) δ 1.09 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 5.12 (d, J = 3.2 Hz, 1 H, OCH), 5.98 (d, J = 3.2 Hz, 1 H, O_2CH), 7.00–7.52 (m, 10 H, C_6H_5).

Benzophenone and 1,3-Dioxole (1a). The reaction mixture was composed of two photoproducts (0.97:1 in benzene; 0.69:1 in acetonitrile). Both products were isolated by means of HPLC with *n*-hexane/ethyl acetate (95/5) as eluate. The major product was identified as benzpinacole[33b] and the minor one as 7,7-diphenyl-2,4,6-trioxabicyclo[3.2.0]heptane, **7a**. ^{1}H NMR (CCl_4) δ 4.57 (d, J = 2.7 Hz, 1 H, OCH), 5.08 (s, 2 H, OCH_2O), 6.07 (d, J = 2.7 Hz, 1 H, O_2CH), 7.13–7.51 (m, 10 H, C_6H_5).

Benzophenone and 4,5-Dimethyl-1,3-dioxole (1d). After irradiation the solvent was removed by distillation. Three products were formed in a 25:5:1 ratio. Benzpinacole[33b] (main product) crystallized upon addition of *n*-hexane/ethyl acetate (95:5) to the residue and was removed by filtration. After filtration over basic aluminum oxide (Woelm) the products were isolated by HPLC. 4-(2,2-Diphenyl-2-hydroxyethyl)-5-methyl-1,3-dioxole, **8** (minor component of mixed adducts): ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 3 H, CH_3), 1.74 (s, 2 H, CH_2), 2.40 (s, 1 H, OH), 5.09 and 5.38 (2 s, 2 H, CH_2O), 7.07–7.80 (m, 10 H, C_6H_5).

4-(Diphenylhydroxymethyl)-4-methyl-5-methylene-1,3-dioxolane (9) (main component): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 3 H, CH_3), 2.81 (s, 1 H, OH), 4.02 and 4.38 (2 d, J = 1.8 Hz, 2 H, $=CH_2$), 4.47 and 4.90 (2 d, J = 1.2 Hz, 2 H, OCH_2O), 7.03–7.83 (m, 10 H, C_6H_5).

Benzil and 4,5-Dimethyl-1,3-dioxole (1d). Only two products were formed in a 3.5:1 (1:0.9) ratio in benzene (acetonitrile). A pinacole from benzil could not be detected, even by comparing with an authentic sample.[33c] The products were identified as oxetanes. The stereochemistry was assigned in analogy to the exo and endo oxetanes which had been obtained from **1d** and 1-phenyl-1,2-propandione.[17b]

7-(*exo*-Benzoyl)-7-phenyl-1,5-dimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (10a): major adduct in benzene; colorless oil; ^{1}H NMR ($CDCl_3$) δ (CCl_4) 1.40 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 4.55 and 4.90 (2 s, 2 H, OCH_2O), 7.15–7.73 (m, 8 H, C_6H_5), 7.92–8.13 (m, 2 H, *o*-C_6H_5). **7-(*endo*-Benzoyl)-7-phenyl-1,5-dimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (10b):** minor adduct in benzene; colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 4.70 and 5.09 (2 s, 2 H, OCH_2O), 7.07–7.47 (m, 6 H, C_6H_5), 7.59–7.93 (m, 4 H, *o*-C_6H_5).

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Appendix

According to Scheme I the rate constant for quenching of the excited ketone is given by eq 5.

$$k_q = \frac{k_1(k_2 + k_3 + k_4)}{k_{-1} + k_2 + k_3 + k_4} \tag{5}$$

The free enthalpy for exciplex formation is defined by eq 6.

$$K_{ex} = \frac{k_1}{k_{-1}} = \exp\frac{-\Delta G_{ex}}{RT} \tag{6}$$

ΔG_{ex} depends on ΔG_2 and the slope of the plot of log k_q vs. ΔG_2 according to eq 7.[4a,22]

$$\Delta G_{ex} = s\Delta G_2/17\ \mathrm{eV}^{-1} \tag{7}$$

The free activation enthalpy for exciplex formation ($\Delta G_1^{\ddagger}$) which is needed for the calculation of k_q according to eq 5 was obtained in analogy with the calculation of $\Delta G_2^{\ddagger}$ by Rehm and Weller.[18a]

$$\Delta G_1^{\ddagger} = \frac{\Delta G_{ex}}{2} + \left[\left(\frac{\Delta G_{ex}}{2}\right)^2 + \Delta G_1^{\ddagger}(0)^2\right]^{1/2} \tag{8}$$

$$k_2 = k_{20} \exp(-\Delta G_2^{\ddagger}/RT) \tag{9}$$

$$\Delta G_2^{\ddagger} = \frac{\Delta G_2}{2} + \left[\left(\frac{\Delta G_2}{2}\right)^2 + \Delta G_2^{\ddagger}(0)^2\right]^{1/2} \tag{10}$$

Registry No. 1a, 288-53-9; **1b**, 22945-10-4; **1c**, 14738-96-6; **1d**, 85976-13-2; **1e**, 85976-14-3; **2a**, 40923-93-1; **2b**, 2678-54-8; **2c**, 109-92-2; **2d**, 26327-98-0; **2e**, 563-79-1; **2f**, 40237-72-7; **3**, 543-75-9; **4**, 110-87-2; **5a**, 110-83-8; **5b**, 591-49-1; **6**, 693-89-0; biacetyl, 431-03-8; benzophenone, 119-61-9; benzil, 134-81-6.

External Heavy-Atom Effects on First and Second Order Decay Rate Constants of Anthracene Triplets

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Abstract: Second order rate constants for quenching of anthracene triplets, $^3A^*$, by methyl iodide, MeI, in benzene and ethyl iodide, EtI, in methylcyclohexane, determined flash kinetically, are $(3.3_0 \pm 0.2_7) \times 10^2$ and $(4.4_6 \pm 0.3_2) \times 10^2$ $M^{-1}\ s^{-1}$ at 25 ± 2 °C. Use of ferrocene, Fe, as a second quencher in methylcyclohexane leads to strictly additive quenching, $k_{Fe} = (5.0_8 \pm 0.14) \times 10^9$ $M^{-1}\ s^{-1}$, and, contrary to an earlier report, provides no kinetic evidence for the intervention of an A/EtI triplet exciplex. $^3A^*$ quenching by ground-state anthracene (self-quenching), $k_{sq} = (2.77 \pm 0.09) \times 10^5$ $M^{-1}\ s^{-1}$, and by MeI are also strictly additive processes in benzene, providing no kinetic evidence for the intervention of a sufficiently long-lived triplet excimer in the self-quenching process. A pronounced increase in the efficiency of A triplet–triplet annihilation observed with [MeI] $\gtrsim$ 2 M in benzene provides strong evidence for interconversion of quintet, triplet, and singlet sublevels of the triplet encounter pairs through heavy–atom enhanced spin–orbit coupling.

It is well established by spectroscopic observations that interaction of solute molecules with molecules containing heavy atoms increases the probabilities of radiative and nonradiative singlet–triplet transitions.[1] This phenomenon is known as the external heavy-atom (Kasha[2]) effect and is attributed to enhanced spin–orbital coupling. In photochemistry, the external heavy-atom (H-A) effect on $S_1 \rightarrow T$ intersystem crossing has been shown to reduce yields of singlet-derived products while enhancing yields of triplet-derived products.[3] At high mol % of H-A addend, triplet product quantum yields decrease due to significant, though less

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Table I. Effects of [A] and [MeI] on k_1 and κ in Benzene[a]

run no.	[A] × 10^3, M	T, °C	$k_1 \times 10^{-2}$, s^{-1}	$\kappa \times 10^{-3}$, s^{-1}	[A] × 10^3, M	[MeI], M	T, °C	$k_{1,0}' \times 10^{-2}$, s^{-1}	$\kappa' \times 10^{-3}$, s^{-1}
1a	0.96_3	$24._5$	3.32	6.06	0.87_9	0.99_6	$25._6$	6.04	7.32
1b	0.99_0	$22._6$	3.11	5.97	0.93_2	0.78_2	$23._6$	5.43	7.3^b
1c	1.06	$25._8$	3.33	6.77	0.89_6	1.98	$26._1$	7.31	7.48
1d	1.14	$25._0$	3.44	6.94	0.89_6	2.87	$25._9$	11.0	8.96
1e	1.17	$27._7$	4.06	6.47	0.96_0	1.78	$27._4$	7.79	7.15
1f	1.17	$25._0$	3.88	6.19	1.04	3.21	$25._0$	14.2	8.82
1g	1.20	$26._0$	4.03	6.33	0.84_1	4.79	$25._3$	20.6	11.02
1h	1.39	$25._5$	4.92	5.61	0.94_1	4.89	$27._6$	19.5	12.16
1i	2.00	$24._6$	5.68	6.40^b	1.90	0.78_2	$26._3$	7.74	6.9^b
1j	2.17	$25._8$	5.82	7.21					
1k	2.17	$25._8$	5.99	6.71	1.98	$0.58_7{}^c$	$25._9$	7.70	6.8^b
1ℓ	4.05	$26._3$	12.18	5.95	3.86	0.78_2	$26._1$	13.2	7.52
1m	5.75	$24._3$	16.24	5.62	5.45	0.78_2	$23._8$	17.5	6.9^b
		av 25.3 (9)		6.32 (42)			25.7 (9)		

[a] Uncertainties in individual k_1, κ, and κ' values estimated by summation of deviations from the mean, $\bar{x}$ [$s = (\sum_{i=1}^{n}(x_i - \bar{x})^2)^{1/2}(n-1)$], were generally smaller than ±5%; standard deviations in $k_{1,0}$ values were generally smaller than ±3%. [b] κ or κ' was fixed to this value inthe fitting procedure. [c] EtI.

pronounced, H-A enhancement of the $T_1 \rightarrow S_0$ decay rate.[3] The photochemical H-A effects were first demonstrated in photodimerization[3,4] and (later) in cross-adduct formation[5] of acenaphthylene.

Qualitative observations indicating similar H-A effects on the photochemistry of anthracene/1,3-diene systems[6] were confirmed by our quantitative study of the effect of [MeI] on A/*trans*,-*trans*-2,4-hexadiene cross-adducts quantum yields in benzene.[7] An earlier spectroscopic study, indicating that the quenching of $^1A^*$ fluorescence by EtI in cyclohexane leads quantitatively to $^3A^*$ whose lifetime is shortened as [EtI] is increased,[8] appeared to confirm the functioning of H-A induced $S_1 \rightarrow T$ and $T_1 \rightarrow S_0$

$$^1A^* + RI \xrightarrow{k_{ha}^S} {}^3A^* + RI \quad (1)$$

intersystem crossing in A thus accounting for the photochemical

$$^3A^* + RI \xrightarrow{k_{ha}^T} {}^1A + RI \quad (2)$$

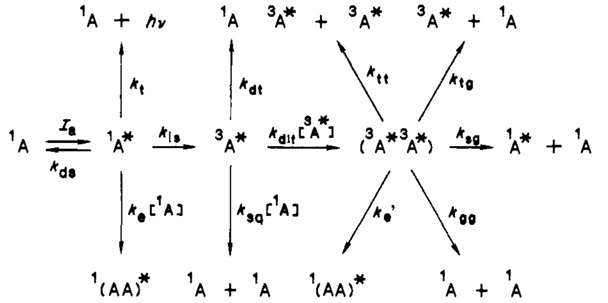
observations. However, the range of $k_{ha}^T = (5.5\text{–}7.1) \times 10^2\ M^{-1}\ s^{-1}$ estimated from the dependence of adduct quantum yields on [MeI] in benzene[7] was much smaller than values reported for EtI in cyclohexane, $k_{ha}^T = 6.95 \times 10^4\ M^{-1}\ s^{-1}$,[8] and in methylcyclohexane, $k_{ha}^T = 5.35 \times 10^3\ M^{-1}\ s^{-1}$.[9] The present flash-kinetics investigation was undertaken in part to resolve the discrepancy in the k_{ha}^T values and to determine whether H-A induced spin-orbit coupling increases the efficiency of triplet-triplet annihilation (TTA).[10]

$$(^3A^{*3}A^*) + RI \xrightarrow{k_{ha}^{TT}} 2\,^1A + RI \quad (3)$$

Kinetics and Results

In the absence of alkyl iodides Scheme I has been used to represent the photophysical processes leading to triplet formation and decay for anthracene.[10,11] Applying the steady-state approximation on $^1A^*$ and $(^3A^{*3}A^*)$ and assuming $I_a = 0$, following flash excitation, gives

Scheme I. Kinetics for Triplet Formation and Decay



^1A, ground-state singlet anthracene; $^1A^*$, lowest excited singlet state; $^3A^*$, lowest triplet state; $^1(AA)^*$, singlet excimer; $(^3A^{*3}A^*)$ paired states resulting from the encounter of two $^3A^*$

$$-\frac{d[^3A^*]}{dt} = k_{dt}[^3A^*] + k_{dif}(2 - p_t - p_s\phi_{is})[^3A^*]^2 \quad (4)$$

where k_{dt} represents all first-order and pseudo-first-order $^3A^*$ decay processes, $p_t = (2k_{tt} + k_{tg})/(k_{tt} + k_{tg} + k_{sg} + k_{gg} + k_e')$ and $p_s = k_{sg}/(k_{tt} + k_{sg} + k_{gg} + k_e')$ are the probabilities that triplet encounter pairs will give $^3A^*$ and $^1A^*$ directly, and $\phi_{is} = k_{is}/(k_{ds} + k_f + k_{is} + k_e[^1A])$ is the intersystem crossing yield of $^1A^*$. Following common practice we let $k_1 = k_{dt}$ and $k_2 = k_{dif}(2 - p_t - p_s\phi_{is})$. Integration of eq 4 and substitution of $^3A^*$ absorbances, A, for concentration terms gives

$$A_t = k_1A_0/\{(k_1 + \kappa A_0)e^{k_1t} - \kappa A_0\} \quad (5)$$

where $A_0 = \epsilon_t[^3A^*]_0l$ is the absorbance of $^3A^*$ at an arbitrary zero time, A_t is the absorbance at a later time t, and $\kappa = k_2/\epsilon_tl$. Transient measurements were recorded at ambient temperature, 25 ± 2 °C, using a 6-nm band-pass centered at 429 and 421 nm for benzene and methylcyclohexane solutions, respectively. Values of k_1, κ, and A_0 were determined by iteratively fitting the predicted values of A_t from eq 5 to the observed values of A_t, using the general least-squares computer program BMDPAR.[12] In each experiment, the decay of $^3A^*$ was measured in rigorously degassed benzene or methylcyclohexane, one or two quenchers were admitted sequentially into the solution through break-seals, and decay measurements were repeated. The quenchers increased k_1 to k_1' and for high [RI] κ to κ'. Since the parameters k_1 and κ are coupled, refinement of parameter determination was achieved by fixing the value of κ to the average from analysis of several flashes

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Table II. Effects of [EtI] or [Fe] on k_1 in Methylcyclohexane[a]

run no.	[A] × 10^4, M	T, °C	$k_1 \times 10^{-2}$, s^{-1}	$\kappa \times 10^{-3}$, s^{-1}	[A] × 10^4, M	[EtI], M	[Fe] × 10^7, M	$k_{1,0}' \times 10^{-2}$,[b] s^{-1}
2a	1.02	25.$_2$	1.70	5.56	0.97$_8$	0.415		3.71
2b	1.03	26.$_2$	1.62	5.55	0.98$_3$	0.355		3.55
2c	1.03	26.$_5$	1.62	5.67				
2d	1.14	25.$_6$	1.58	5.71	1.01	0.77$_5$		5.62
2e	1.08	26.$_5$	1.74	5.74	1.07		2.07	12.4
2f	1.20	24.$_1$	1.61	6.01	1.14		2.20	13.2
2g	1.24	24.$_4$	1.90	5.78	1.15		2.13	12.6
2h	1.28	25.$_6$	1.63	6.91	1.08	1.55$_5$		8.30
2i[c]	1.21	24.$_2$		6.40			2.22	11.8
2j[c]	1.30	25.$_8$		5.68			2.35	13.2
		av 25.4 (8)		5.79 (19)				

[a] See footnote *a*, Table I. [b] For EtI samples κ was fixed to the corresponding unquenched value; for Fe samples $\kappa = 5.8 \times 10^3$ s^{-1} was employed, $k_{1,n}'$ was independent of n and average k_1' values are listed. [c] Initial solution contained both A and Fe.

Table III. Effects of [EtI] and [Fe] Together on k_1 in Methylcyclohexane[a]

run no.[b]	[A] × 10^4, M	[EtI], M	[Fe] × 10^7, M	T, °C	$k_{1,0}' \times 10^{-2}$,[c] s^{-1}
2e	1.03	0.348	2.01	26.$_8$	13.3$_2$
2g	1.04	0.761	2.00	25.$_5$	15.9$_1$
2i	1.01	1.192	2.00	25.$_0$	15.5$_6$
2j	1.05	1.59	2.04$_5$	26.$_5$	18.2$_1$
				av 26.0 (7)	

[a] See footnote *a*, Table I. [b] Continuation of corresponding runs in Table II. [c] $\kappa = 5.8 \times 10^3$ s^{-1} was employed.

and adjusting k_1 and A_0. It was generally found that k_1 and k_1' are independent of the number of flashes for A alone or in the presence of ferrocene, Fe, but that in the presence of MeI or EtI k_1' steadily increases with each additional flash. Fortunately, for constant flash energy, $k_{1,n}'$, the k_1' value corresponding to the nth flash, was linearly dependent on n (slopes varied from 13 to 130 s^{-1}/flash, but most clustered at 55 s^{-1}/flash and were relatively smaller, 30 s^{-1}/flash in solutions containing Fe in addition to EtI) so that $k_{1,0}'$ values could readily be obtained from the intercepts of such plots. Values of k_1 and κ as a function of [A] and $k_{1,0}'$ and κ' values as a function of [A] and of [MeI] in benzene are shown in Table I. The effects of [EtI] and [Fe] on k_1 in methylcyclohexane, included separately and together, are shown in Tables II and III, respectively.

Discussion

In the absence of quenchers, the first order decay rate constant of $^3A^*$, k_1, includes unimolecular radiative, k_p, and nonradiative, k_{nr}, decay constants in addition to the pseudo-unimolecular self-quenching rate, $k_{sq}[^1A]$. If the latter process is assumed to involve triplet excimer (or intimate encounter pair) formation

$$^3A^* + {}^1A \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} {}^3(AA)^* \xrightarrow{k_{ed}} 2\,{}^1A \qquad (6)$$

then $k_1 = k_1^0 + (k_{dif}/k_{-dif})k_{ed}[^1A]$ is expected where $k_{ed} \ll k_{-dif}$, $k_{sq} = (k_{dif}/k_{-dif})k_{ed}$, and $k_1^0 = k_p + k_{nr}$.[11] The upper limit for $k_1^0 = 49$ s^{-1} is established by the lowest k_1 values obtained experimentally for dilute A solutions ($\sim 10^{-6}$ M) in hydrocarbon solvents at room tempeature,[11,13,14] and the lower limit, $k_1^0 = 27.6 \pm 0.7$ s^{-1}, corresponds to the observed k_1 value in a glassy hydrocarbon medium at 77 K[15] (somewhat lower k_1 values have been observed in alcoholic glasses at 77 K, e.g., $k_1 = 24 \pm 1$ s^{-1} in EPA[14]). Since the radiative rate constant for unperturbed $^3A^*$, $k_p = (5.6 \pm 3) \times 10^{-3}$ s^{-1}, estimated from the $S_1 \rightarrow T$ intersystem crossing yield, ϕ_{is} (assumed equal to $1 - \phi_f$), the phosphorescence quantum yield, ϕ_p, and triplet lifetime at 77 K in ethanol,[16] is negligibly small, k_1^0 reflects almost exclusively the nonradiative rate constant. It follows that 28 $s^{-1} \leq k_{nr} \leq 49$ s^{-1} for the 77–298 K temperature range. Reported values for k_{sq} at 23 °C in benzene and cyclohexane as solvents are $3.1_9 \times 10^5$ and $1.0_6 \times 10^6$ M^{-1} s^{-1}, respectively.[11]

The k_1 values in Tables I and II are in good agreement with the literature data reviewed above. A plot of k_1 vs. $[^1A]$ in benzene (excluding runs 1e, 1f, 1g, 1i) gives $k_1^0 = 41.8 \pm 25.3$ and $k_{sq} = (2.77 \pm 0.09) \times 10^5$ M^{-1} s^{-1} at 25.3 ± 0.9 °C. With the k_1 values adjusted to 23.0 °C using the activation parameters for k_{sq} in ref 11 the same plot gives $k_1^0 = 34.1 \pm 27.2$ and $k_{sq} = (2.63 \pm 0.10) \times 10^5$ M^{-1} s^{-1}. The k_1^0 values are within experimental error of k_1^0 at 77 K[15] and a series of values estimated for several solvents at higher temperature in ref 14. The k_{sq} value is about 20% smaller than that from our previous determination[11] and is considered more reliable since it derives from many more independent experiments with extreme care having been taken to ensure rigorous degassing. With methylcyclohexane as solvent, a rather narrow range of [A] was employed (Table II). Agreement with previous work[11,13,17] was established by adjusting the k_1 values in Table II to 23 °C with use of the activation parameters for k_{sq} in cyclohexane and substracting the expected k_q[A] term from the adjusted k_1 values to obtain $k_1^0 = 50 \pm 7$ s^{-1}.[11]

H-A Effect on $^1A^*$ Decay. Measurements of the quenching of $^1A^*$ fluorescence by RI indicate that k_{ha}^S, eq 1, is $^1/_2 k_{dif}$. With MeI in benzene $k_{ha}^S = 5.5 \times 10^9$ M^{-1} s^{-1} at 23 °C was obtained from the Stern–Volmer plot for [MeI] up to 1.2 M.[7] However, if the slight upward curvature in the plot is assumed to be real, a somewhat lower $k_{ha}^S = 3.9 \times 10^9$ M^{-1} s^{-1} can be based on the initial slope. The latter value is very close to $k_{ha}^S = 3.96 \times 10^9$ M^{-1} s^{-1} obtained for EtI in cyclohexane ([EtI] ≤ 0.13 M).[8] Independent studies have yielded $k_{ha}^S = 4.2 \times 10^9$ and 3.4×10^9 M^{-1} s^{-1} for MeI and EtI, respectively, in cyclohexane[18a] and $k_{ha}^S = 3.5 \times 10^9$ M^{-1} s^{-1} for EtI in n-heptane.[18b]

It has been claimed that k_{ha}^S for EtI in cyclohexane is smaller for degassed than for air-saturated solutions, suggesting the intermediacy of an $^1A^*$/EtI exciplex which is formed reversibly and is quenched by oxygen.[19] The delayed fluorescence of n-butyl bromide (1–8 M) includes an emission band in the 540-nm region which has been assigned to $^1(A{\cdot}n\text{-BuBr})^*$ exciplex emission.[20] Accordingly, $k_{ha}^S = k_{dif}k_{ha}^{se}/(k_{ha}^{se} + k_{diss})$ where k_{ha}^{se} and k_{diss}

$$^1A^* + RI \underset{k_{diss}}{\overset{k_{dif}}{\rightleftharpoons}} {}^1(A{\cdot}RI)^* \xrightarrow{k_{ha}^{se}} {}^3(A{\cdot}RI)^* \rightarrow {}^3A^* + RI \qquad (7)$$

are the H-A induced intersystem crossing and dissociation rate

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constants of the *s*inglet *e*xciplex. Since $k_{ha}^{S} \simeq {}^1/_2 k_{diff}$, it follows that $k_{ha}^{se} \simeq k_{dis} \lesssim 10^{11}$ s^{-1}.[21]

DeToma and Cowan[8] employed the method of Medinger and Wilkinson[22] to calculate ϕ_{is} for $^1A^*$ and thus established that, at least for EtI in cyclohexane, the H-A interaction in eq 1, or its more detailed version, eq 7, leads quantitatively to $^3A^*$. Using eq 5 and the derived parameters we calculated ratios of anthracene triplet concentrations before, $[^3A^*]_0$, and after, $[^3A^*]_{ha}$, MeI addition for [MeI] ≥ 1.78 M in benzene (corresponding to quenching of ≥97% of prompt ^1A fluorescence) at peak flash intensity (3 μs). We find $([^3A^*]_{ha}/[^3A^*]_0) = 1.26 \pm 0.06$ consistent with a significant increase in the yield of $^3A^*$ in the presence of MeI. Since our excitation flash is rather broad (20 μs peak width at half height), it is unlikely that the deviation of this ratio from $\phi_{is}^{-1} = 1.37 \pm 0.02$ expected from eq 1 or 7 is significant.[8,10]

H-A Effects on $^3A^*$ Decay, k_1. H-A enhanced spin–orbit coupling should, in principle, increase k_1 by increasing radiative and radiationless $T_1 \rightarrow S_0$ intersystem crossing rate constants and, if the triplet excimer is sufficiently long-lived, by increasing the efficiency of the self-quenching process.

Spectroscopic studies at 77 K in glassy media have revealed a pronounced increase in the phosphorescence quantum yields, ϕ_p, of aromatic hydrocarbons when an alkyl halide is included in the medium. A striking example is provided by naphthalene in ethanol–methanol (EM 4:1, v/v) glasses. Replacement of $^1/_4$ of the solvent with *n*-propyl halide leads to progressively lower ϕ_f's and higher ϕ_p's as the halogen is changed from Cl to Br to I.[23,24] The analysis by Birks[23b] of the data in ref 24a suggests strongly that the H-A effect under these conditions is much more pronounced on the radiative rate constant (5.6-fold increase in k_p for *n*-PrI) than on the radiationless decay constant of naphthalene triplets (1.4-fold increase in k_{nr} for *n*-PrI). The observation that ϕ_p for anthracene in *n*-butyl alcohol increases ~5-fold with increasing [*n*-BuBr] (1–8 M) suggests that the H-A effect favors k_p over k_{nr} at room temperature as well.[20]

The effect of EtI on k_p for A at room temperature can be estimated from the enhanced absorptivities of the $S_0 \rightarrow T_1$ transition in EtI as solvent with use of the approximate relationship

$$k_p^{-1} \simeq 3.47 \times 10^8 (\tilde{\upsilon}_A{}^2 n^2)^{-1} (g_u/g_l) \left(\int \epsilon_{S_0 \rightarrow T1}\, d\tilde{\upsilon} \right)^{-1} \quad (8)$$

where ϵ is the absorptivity, $\tilde{\upsilon}_A$ is the maximum of the absorption band, n is the refractive index of the medium, and g_u (=3) and g_l (=1) are the multiplicities of upper and lower states, respectively.[25,26] If, in addition, we assume similar spectral shapes for $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ transitions, eq 8 can be used to relate k_p in EtI to the well-known value of $k_f = 6.43 \times 10^7$ s^{-1} in benzene,[27] where $\tilde{\nu}_A$ = 26 400 and 14 820 cm^{-1} are 0–0 band frequencies for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions, respectively, and $\epsilon_{S_0 \rightarrow T} \simeq$

$$k_p \simeq k_f \frac{(\tilde{\upsilon}_A{}^2)_{S_0 \rightarrow T_1} \epsilon_{S_0 \rightarrow T_1}}{3(\tilde{\nu}_A{}^2)_{S_0 \rightarrow S_1} \epsilon_{S_0 \rightarrow S_1}} \quad (9)$$

0.010 and $\epsilon_{S_0 \rightarrow S_1} = 8.2 \times 10^3$ M^{-1} cm^{-1} are the absorptivities at $\tilde{\upsilon}_{max}$ for the two transitions in EtI and benzene, respectively (n is the same for these solvents).[25,27] Substitution of these quantities into eq 9 gives $k_p^{ha} \simeq 8.2$ s^{-1}, indicating that, despite an impressive H-A enhancement factor of 1.5 × 10^3, the phosphorescence rate constant contributes little to the overall $k_{1,0}'$ values lited in Tables I and II.

The increase in k_1' with increasing number of flashes is probably associated with the generation of quenching impurities from the photochemical decomposition of RI. Spectroscopic evidence has been presented for the formation of I_2 upon exposure of EtI solutions to weak sunlight.[25] Though handling of RI solutions in our experiments was carried out in the dark and RI is transparent at the monitoring wavelengths for TT absorption, it was not possible to avoid some light exposure (and/or A* sensitized decomposition) during flash excitation of the samples. However, the extrapolated $k_{1,0}'$ values should reflect the true H-A effect in the absence of decomposition.

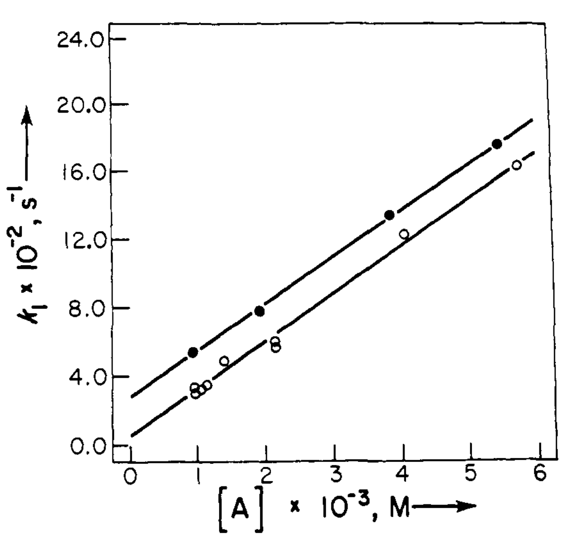

Figure 1. The dependence of k_1 on [A] in the absence (○) and in the presence (●) of 0.782 M MeI in benzene.

In order to evaluate the effect of RI on $k_{1,0}'$ it is first necessary to determine whether cooperative quenching events lead to an

$$^3(AA)^* + RI \xrightarrow{k_{ha}^{ed}} 2^1A + RI \quad (10)$$

$$^3(A{\cdot}RI)^* + {}^1A \xrightarrow{k_{ha}^{ed'}} 2^1A + RI \quad (11)$$

increase in quenching constants. Kinetic manifestations of intervention of eq 10 and/or 11 would be non-additive quenching of $^3A^*$ by ^1A and RI.[9,28] For example, inclusion of eq 10 as a triplet excimer decay step modifies k_{sq} to $k_{ha}^{sq} = k_{dif}(k_{ed} + k_{ha}^{ed}[RI])(k_{-dif} + k_{ed} + k_{ha}^{ed}[RI])^{-1}$ which reduces to $k_{ha}^{sq} = (k_{dif}/k_{-dif})(k_{ed} + k_{ha}^{ed}[RI])$ if the reasonable assumption $k_{-dif} \gg (k_{ed} + k_{ha}^{ed}[RI])$ is applied. Runs 1b, 1i, 1ℓ, and 1m with $[CH_3I] = 0.78_2$ M and varying [^{1}A], Table I, allow a test of this possibility. A plot of $k_{1,0}'$ vs. [^{1}A] for these runs (Figure 1) gives a line which is parallel to that obtained in the absence of MeI, slope = k_{ha}^{sq} = (2.70 ± 0.04) × 10^5 M^{-1} s^{-1} and intercept = $k_1^0 + k_{ha}^T$[MeI] = 279 ± 16 s^{-1} at 25.0 ± 1.3 °C. It follows that $k_{sq} = k_{ha}$ and that at least for [RI] ≤ 0.78$_2$ M eq 10 does not contribute in the decay mechanism. It appears that the triplet excimer or encounter complex is too short-lived to allow H-A enhanced spin–orbit coupling to contribute to its decay.

Since k_1^0 must be in the 28–49-s^{-1} range, the intercept of the MeI line gives $k_{ha}^T = (3.1 \pm 0.3) \times 10^2$ M^{-1} s^{-1}. This rate constant can be evaluated more accurately from a plot of $k_{1,0}' - k_1$ vs. [MeI] (Table I, Figure 2).[29] The slope of the least-squares line through zero for all low [^{1}A] runs, except lc, gives $k_{ha}^T = (3.3_0 \pm 0.2_7) \times 10^2$ M^{-1} s^{-1}. We conclude that $^3A^*$ quenching by ^1A and MeI remains strictly additive up to 4.9 M [MeI]. The data in Table I are inconsistent with the functioning of "termolecular" quenching steps 10 and 11.

The k_{ha}^T value for MeI in benzene is in reasonable agreement (ca. a factor of 2 smaller) with the approximate value estimated from steady-state irradiation quantum yield measurements for

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(23) (a) Ref 1b, p 317. (b) Ref 1c, pp 210–211, 266.

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(27) Reference 7 and references cited therein.

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(29) The k_1 values were adjusted to account for the small decreases in [^{1}A] upon admission of quencher into the solutions.

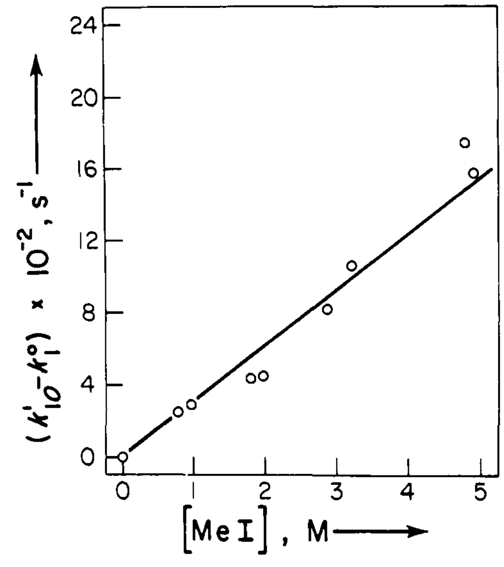


Figure 2. The dependence of k_1 on [MeI] in benzene.

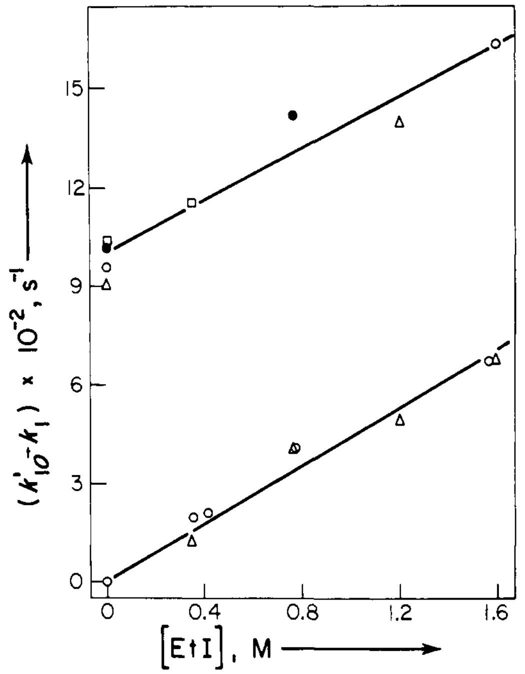
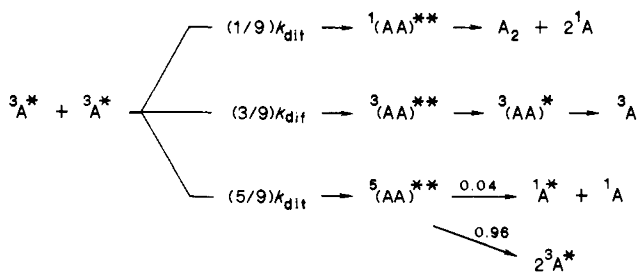


Figure 3. The dependence of k_1 on [EtI] in the absence, lower line, and in the presence, upper line, of 2.00 × 10^{-7} M ferrocene in methylcyclohexane. On the upper line different symbols are employed for each run. Upper line points corrected for the Fe effect are shown as Δ on the lower line.

anthracene/2,4-hexadiene cross-adducts.[7] Complications in the photochemical measurements due to possible MeI decomposition were not suspected and were neglected in the treatment of the quantum yields. However, the discrepancies between this rate constant and earlier values obtained for EtI in cyclohexane ($k_{ha}{}^T$ = 6.95 × 10^4 M^{-1} s^{-1})[8] and in methylcyclohexane ($k_{ha}{}^T$ = 5.35 × 10^3 M^{-1} s^{-1})[9] appeared much too large to be attributed to the solvent change. The measurements summarized in Tables II and III were conducted in order to resolve the discrepancy. Values of ($k_{1,0} - k_1$), calculated as described for benzene solutions, are plotted vs. [EtI] in Figure 3. The slope of the least-squares line through zero as intercept gives $k_{ha}{}^T = (4.6_4 \pm 0.4_1) \times 10^2$ M^{-1} s^{-1} at 25.4 ± 0.8 °C, which though somewhat larger than $k_{ha}{}^T$ for MeI in benzene, cf. also run 1k, is more than an order of magnitude smaller than the smallest previous value.[9] If the line in Figure 3 can be extrapolated to neat EtI (~12.4 M), as is suggested by the results with MeI in benzene, the maximum H-A enhanced rate constant for radiationless deactivation of $^3A^*$ would

Scheme II. Mechanism for Anthracene TTA



be given by ($k_{ha}{}^T$[EtI] − $k_p{}^{ha}$) = 5.8 × 10^3 s^{-1}. This represents a 200-fold enhancement over the minimum unperturbed $k_{nr} \simeq$ 28 s^{-1} value.[15] Since the corresponding H-A enhancement for radiative $^3A^*$ decay is 1.5 × 10^3 (see above), we predict a nearly 10-fold enhancement of the phosphorescence quantum yield of A in degassed neat EtI.[30] This prediction is consistent with low-temperature observations in glassy media,[23,24] as well as with the enhanced phosphorescence observed at room temperature in solutions containing bromoalkanes.[21,31]

Enhanced quenching of $^3A^*$ by EtI in the presence of a constant amount of Fe had led to the conclusion that in addition to competitive quenching of $^3A^*$ by the two quenchers, eq 2 and 12, Fe

$$^3A^* + {}^1Fe \xrightarrow{k_{fe}} {}^1A + {}^3Fe^* \qquad (12)$$

is an efficient quencher of the triplet exciplex $^3(A\cdot EtI)^*$.[9] Our

$$^3A^* + EtI \overset{K_e}{\rightleftarrows} {}^3(A\cdot EtI)^* \xrightarrow{k_{fe}'[Fe]} {}^1A + EtI + {}^3Fe^* \qquad (13)$$

observation of a much smaller $k_{ha}{}^T$ value for EtI than was reported in ref 9 renders the interpretation of the reported Fe effect ambiguous. Since the dominant quenching event in the absence of Fe would now have to be ascribed to an impurity in EtI, it would be just as likely that Fe's non-additive quenching involves interception of an exciplex of $^3A^*$ with the impurity. For this reason, the Fe experiments described in ref 9 were repeated under our conditions (Tables II and III). The rate constant k_{fe} for triplet excitation transfer from $^3A^*$ to Fe, eq 12, can be calculated from the data for runs 2e, 2f, 2g, 2i, and 2j, Table II, $k_{fe} = (k_1' - k_1)/[Fe]$.[29,31] The range of the five independent values is (4.5–5.2) × 10^9 M^{-1} s^{-1}, and excluding the lowest value (run 2i) gives k_{fe} = (5.08 ± 0.14) 10^9 M^{-1} s^{-1} which is about a factor of 2 smaller than the previously reported value in methylcyclohexane,[9] but agrees well with k_{fe} = 4.4 × 10^9 M^{-1} s^{-1} obtained in benzene at room temperature.[32] The $k_{1,0}'$ values in Table III, expressed both as $k_{1,0}' - k_1$ and as $k_{1,0}' - k_1 - k_{fe}[Fe]$, are plotted vs. [EtI] in Figure 3.[29,33,34] If anything, the Fe line has a somewhat smaller slope [$s = (3.9_7 \pm 0.4_1) \times 10^2$ M^{-1} s^{-1}; i = 1004 ± 29 s^{-1}]. The linearly independent additivity of the EtI and Fe quenching effects becomes especially apparent when each of the four runs in Table III is separately corrected for the Fe effect (on lower line). The least-squares line through both sets of experimental points gives $k_{ha}{}^T = (4.4_6 \pm 0.3_2) \times 10^2$ M^{-1} s^{-1}. Clearly, the data do not require the involvement of an $^3(A\cdot EtI)^*$ exciplex. If this exciplex actually participates in the EtI quenching process, its steady-state concentration must be too small to allow Fe quenching, eq 13, at the Fe concentration employed. Assuming that the fast equilibration limit for exciplex (or encounter complex) formation[35] applies, the experimental uncertainty in the slopes in Figure 3 is sufficient to prevent its detection provided that $K_e \leq 0.08$ M^{-1}. This limiting value is close to that expected for an encounter complex if only

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(30) Experiments to test this prediction are in progress in our laboratory.

(31) Cf. also: Turro, N. J.; Liu, K.-C.; Chow, M.-F.; Lee, P. *Photochem. Photobiol.* **1978**, *27*, 523.

(32) Fry, A. J.; Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4781.

(33) For runs 2i and 2j, k_1 = 50 + (1.09 × 10^4)[^{1}A] was employed, see above and ref 11.

(34) The $k_{1,0}' - k_1$ values were adjusted to account for the small deviations of [Fe] from 2.00 × 10^{-7} M.

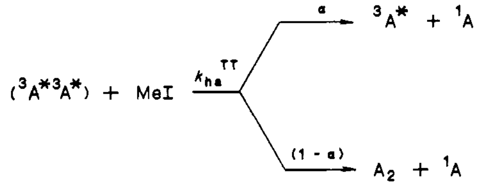
(35) Reference 1c, pp 309–311.

cratic entropy is considered: $K_e = (k_{dif}/k_{-dif}) = [S]^{-1} \simeq 0.10$, where [S] is the molarity of the solvent.[21]

The H-A Effect on κ. A detailed flash-kinetics study of the temperature dependence of κ for $^3A^*$ in toluene and benzene established that $k_2 = 0.57\ k_{dif}$ over the experimental range of T/η.[10,36] From the relationship $(2 - p_t - p_s\phi_{is}) = 0.57$ and independent determinations of $p_s = 0.046$ (delayed fluorescence in ethanol)[10,38] and $\phi_{is} = 0.72$,[8,22] $p_t = 1.40$ was obtained.[10] This high inefficiency in TTA was nicely accounted for by the mechanism in Scheme II which is based on spin-statistical considerations.[10] The formation of dimer from the singlet encounter pair[39] and the dissociative nature of the triplet excimer (only one in $\sim 10^5$ encounters of $^3A^*$ with ^1A leads to quenching)[11] have been confirmed since this proposal. If, in addition, all quintet pair states give back two triplets, $p_t = 1.44$ is predicted. The small yield of singlets from the quintet was tentatively proposed to account for delayed fluorescence and the somewhat smaller experimental p_t value.[10] Of course, some delayed fluorescence could arise by dissociation of the singlet excimer, but this possibility is inconsistent with analyses of fluorescence quenching and photodimerization results.[10,39]

Since the simple spin-statistical mechanism (Scheme II) nicely predicts p_t and p_e', the fraction of TT encounters leading to the dimer precursor,[39] we are inclined to accept the underlying premise that, for anthracene, $(^3A^{*3}A^*)$ spin states with different multiplicities do not interconvert appreciably. In principle, spin-orbit coupling induced by external H-A addents acting on such encounter pairs could alter the mechanism of TTA by opening interconversion pathways. Some experimental evidence supporting this hypothesis is provided by the dependence of $^1A^*$ delayed fluorescence intensity in *n*-butyl alcohol on [*n*-BuBr].[20] After an initial sharp drop in intensity, the fluorescence intensity, adjusted to constant $[^3A^*]$, rises slowly with increasing [*n*-BuBr] in the 2–8 M range.[20] It appears that the quenching of kinetically free $^1A^*$, eq 1, functions only in the low [*n*-BuBr] range and that at higher concentrations the increased fluorescence reflects an increase in p_s by interaction of $(^3A^{*3}A^*)$ with alkyl halide.[20] Evidence that in several meso-substituted anthracenes high alkyl halide concentrations (seemingly paradoxically) reduced the efficiency of $S_1 \rightarrow T$ intersystem crossing has been presented.[18b,40,41] The origin of this effect has been traced to an increase in the activation energy for intersystem crossing due to the greater stabilization of S_1 than of T by more polar solvents.[41] No such effect has been reported for unsubstituted anthracene, and strong fluorescence quenching was observed at the highest [MeI] employed (1.28 M).[7] Furthermore, the extrapolated initial $[^3A^*]$ values from our flash-kinetics data indicate that the limiting enhanced ϕ_{is} value obtains for $[MeI] \leq 4.9$ M. We, therefore, assume that, for anthracene, S_1 lies sufficiently above T in hydrocarbon solvents that the increase in medium polarity due to alkyl halide addition does not reverse the ordering of the states; i.e., $\phi_{is} \simeq 1.0$ for $0.8 \leq [MeI] \leq 4.9$ M. In addition to possible changes in p_s,[20] our own preliminary observations on the effect of [MeI] on the yield of A_2 in benzene have suggested the possibility that p_e' is also increased by the H-A addend.[7]

The observed increase in κ' with increased [MeI] (Table I) requires that the net result of the interactions of $(^3A^{*3}A^*)$ pairs with MeI be enhanced efficiency of triplet destruction. Although this net result is represented by eq 3, we cannot rule out the possibility that MeI also enhances pathways which give back triplets. Enhancement of p_s would, for example, fall in this latter category when considered together with $\phi_{is} = 1.0$ as discussed above. Accordingly, a more general form of eq 3 is


$$(^3A^{*3}A^*) + MeI \xrightarrow{k_{ha}^{TT}} \begin{cases} \xrightarrow{\alpha} {}^3A^* + {}^1A \\ \xrightarrow{(1-\alpha)} A_2 + {}^1A \end{cases} \qquad (14)$$

where α is the fraction of interactions that ultimately give back triplets and $(1 - \alpha)$ is the fraction of interactions which destroy triplets. Inclusion of eq 14 in Scheme I modifies the term in parentheses in eq 4.

$$k_2 = k_{dif}[2 - (2k_{tt} + k_{tg} + k_{sg} + \alpha k_{ha}{}^{TT}[MeI])/(k_{tt} + k_{tg} + k_{sg} + k_{gg} + k_e' + k_{ha}{}^{TT}[MeI])] \qquad (15)$$

Rearrangement of eq 15 gives

$$r = \frac{1}{p_t + p_s} + \frac{k_{ha}{}^{TT}}{2k_{tt} + k_{tg} + k_{sg}}(1 - \alpha r)[MeI] \qquad (16)$$

where $r = k_{dif}/(2k_{dif} - k_2)$.

The κ' values in Table I were converted to k_2 by assuming that the effective $\bar{\epsilon}_t = 4.93 \times 10^4\ M^{-1}\ cm^{-1}$ in benzene[10] applies also to the MeI solutions (Table IV). Since k_2 is proportional to k_{dif}, some of the observed increase with increasing [MeI] must reflect the attendant decrease in medium viscosity, $\eta = 6.06$ and 4.79 mP at 25 °C for benzene and MeI, respectively.[42] The viscosities of MeI solutions, η_{soln}, estimated assuming ideal behavior ($\eta_{soln} = f_B\eta_B + f_{MeI}\eta_{MeI}$, where f_B and f_{MeI} are mole fractions of benzene and MeI, respectively), were converted to k_{dif} values starting from the expected value of $k_{dif}{}^B = 8.7_4 \times 10^9\ M^{-1}\ s^{-1}$ in benzene at 25 °C:[10,20] $k_{dif}{}^{soln} = k_{dif}{}^B\eta_B/\eta_{soln}$ (Table IV). The r values listed in Table IV were calculated from the corresponding k_2 and k_{dif} values. It can readily be seen that, within our experimental uncertainty, r is essentially independent of [MeI] for [MeI] ≤ 2 M but increases significantly for higher [MeI]. The initial insensitivity of r to [MeI] changes is consistent with our inability to discern changes in κ in the EtI experiments.

According to eq 16, the plot of r vs. [MeI] should be linear for $\alpha = 0$. Actually, the data show pronounced curvature (Figure 4). Nor is linearity improved when r is plotted vs. $(1 - \alpha r)$[MeI] with $\alpha = 0.5$. Unfortunately, due to instrumental limitations our κ' values are not sufficiently precise to allow the conclusion that these deviations from linearity are real. If they were, they could reflect concerted involvement of more than one MeI molecule in the quenching step as, for example, would result if TTA of two $^3(A{\cdot}MeI)^*$ exciplexes were involved, or they could indicate that efficient $(^3A^{*3}A^*)$ quenching requires sequential interactions with MeI, e.g.,

$$^5(AA)^{**} \xrightarrow{MeI} {}^3(AA)^{**} \xrightarrow{MeI} {}^1(AA)^{**} \qquad (17)$$

We also cannot rule out the possibility that static quenching by

Table IV. The Effect of [MeI] on k_2[a]

run no.[b]	[MeI], M	$k_2 \times 10^9$, $M^{-1}\ s^{-1}$	$k_{dif} \times 10^9$, $M^{-1}\ s^{-1}$	r	[MeI](1 − 0.5r), M
	0	4.81[c]	8.74	0.694	0
1ℓ	0.782	5.56	8.87	0.728	0.497
1a	0.996	5.41	8.90	0.718	0.638
1e	1.78	5.29	9.02	0.707	1.154
1c	1.98	5.53	9.05	0.720	1.267
1d	2.87	6.63	9.20	0.782	1.750
1f	3.21	6.52	9.26	0.772	1.971
1g	4.79	8.15	9.49	0.876	2.692
1h	4.89	8.99	9.51	0.948	2.572

[a] See text for definition of r and calculation of k_2 and k_{dif}. [b] See Table I. [c] Average for runs in the absence of MeI.

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(36) The 0.57 factor is subject to a minimum uncertainty of ±0.02 introduced by the uncertainty in p_t.

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(42) Lange, N. A. *Handbook of Chemistry*, 9th ed.; Handbook Publishers, Inc.: Sandusky, OH, 1956; p 1657.

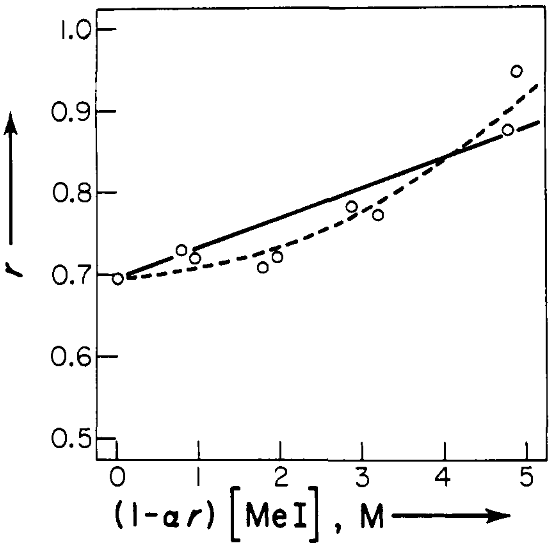

Figure 4. The effect of [MeI] on the efficiency of TTA, eq 16.

MeI plays a role since at the high concentrations required for the observed increase in κ' every TT encounter pair must have one or more MeI nearest neighbors. Future work should certainly address these interesting possibilities. For the present, application of the simple mechanism in eq 14 should suffice. The slope of the least-squares line in Figure 4, forced through the expected intercept, $(p_t + p_s)^{-1} = 0.69_4$,[10] gives $[k_{ha}^{TT}/(2k_{tt} + k_{tg} + k_{sg})] = 0.04$ M^{-1} for $\alpha = 0$; 0.07 M^{-1} is obtained for $\alpha = 0.5$. If we define $\tau_{TT} = (k_{tt} + k_{tg} + k_{sg} + k_{gg} + k_e')^{-1}$ as the effective lifetime of ($^3A^{*3}A^*$) pairs, slope to intercept ratios give $k_{ha}^{TT}\tau_{TT} =$ 0.06–0.10 M^{-1} for $0 \leq \alpha \leq 0.5$.[43] Neglecting static quenching and using $k_{ha}^{TT} \leq k_{dif} \simeq 9 \times 10^9$ M^{-1} s^{-1} gives $\tau_{TT} \geq$ 6.7–11 ps. Accordingly, the minimum effective lifetime of the triplet pair is that expected for a solvent caged encounter complex.

It is of interest to speculate concerning the relationship of the limiting lifetime τ_{TT} to the individual decay rate constants of the singlet, triplet, and quintet encounter pairs in Scheme II (rapid equilibration between sublevels within each multiplicity is assumed with no external applied magnetic fields). According to Scheme II, encounter pairs of different multiplicities do not interconvert and therefore should have independent decay pathways and lifetimes. The magnitude of p_e' has led to the conclusion that all ^{1}(AA)**, the doubly excited singlet encounter pairs, decay via the pericyclic minimum (doubly excited) which is generally accepted as the ultimate precursor to dimer.[39] They may do so either directly, staying within the doubly excited surface, or via internal conversion to ^{1}(AA)*, the singlet excimer (singly excited) followed by reentry into the doubly excited surface. We tentatively prefer the direct pathway since A_2 dimer has been observed at high [MeI].[7] The relatively long singlet excimer lifetime, ~1.5 ns,[44] should lead to efficient quenching by RI which would preclude its involvement in dimer formation at the high [RI] employed. The direct formation of the pericyclic minimum from ^{1}(AA)** and the subsequent decay to dimer and anthracene could, on the other hand, be too fast to allow the functioning of external H-A perturbations on the decay of these species. In Scheme II, the doubly excited triplet pair, ^{3}(AA)**, is proposed to undergo a spin-allowed internal conversion to the triplet excimer, ^{3}(AA)*, which based on the inefficiency of $^3A^*$ self-quenching is expected to mainly dissociate.[10,11] These processes also are likely to be too fast to allow H-A induced quenching. The result in this paper are certainly consistent with no quenching of ^{3}(AA)* since quenching by ^{1}A and by MeI remains additive for [MeI] ≤ 4.9 M. It appears, therefore, that trapping of the normally dissociative quintet encounter pair is the most likely process leading the observed increase in κ'. Accordingly, we tentatively propose that the lifetime of ^{5}(AA)** must be ≳7–11 ps.

Table V. Summary of Rate Parameters

parameter[a]	value	remark	ref
k_f	6.43×10^7 s^{-1}	Scheme I	ref in 38
k_{is}	1.47×10^8 s^{-1}	Scheme I	9, 22, 38
k_p	$(5.6 \pm 3) \times 10^{-3}$ s^{-1}		16
k_{nr}	28–49 s^{-1}	Scheme I (k_{dt})	13–15
k_{sq}	$(2.77 \pm 0.09) \times 10^9$ M^{-1} s^{-1}	eq 6	*b,c*
k_{ha}^S	$(3.9\text{–}5.5) \times 10^9$ M^{-1} s^{-1}	eq 1	8, 9, 18
k_{ha}^{se}	≲10^{11} s^{-1}	eq 7	*b*
k_p^{ha}(EtI)	8.2 s^{-1}	eq 8, 9	25
k_{ha}^T(MeI/B)	$(3.3_0 \pm 0.2_7) \times 10^2$ M^{-1} s^{-1}	eq 2	*b*
k_{ha}^T(EtI/MCH)	$(4.4_6 \pm 0.3_2) \times 10^2$ M^{-1} s^{-1}	eq 2	*b*
k_{Fe}(MCH)	$(5.08 \pm 0.14) \times 10^9$ M^{-1} s^{-1}	eq 12	*b*
$k_{ha}^{TT}\tau_{TT}$	0.06–0.10 M^{-1}	eq 14	*b*
f_{is}	≲6.8×10^2	k_{ha}^{se}/k_{is}	*b*
f_p	~1.5×10^3	k_p^{ha}/k_p	*b*
f_{nr}	~2.0×10^2	k_{ha}^T[RI]$/k_{nr}$	*b*

[a] In benzene, otherwise solvent and/or RI indicated in parentheses. [b] This work. [c] Replaces 3.2×10^9 M^{-1} s^{-1} of ref 11.

Summary. Rate parameters measured or estimated in this work are collected in Table V along with some relevant rate constants from the literature. These parameters allow evaluation of the sensitivities of intersystem crossing processes from $^1A^*$ and $^3A^*$ to external H-A enhancement under conditions normally employed in photochemical studies (solution/room temperature). DeToma and Cowan have formalized such evaluations by defining enhancement factors f.[8] For instance, by using our notation, the sensitivity factor for $S_1 \rightarrow T$ intersystem crossing would be $f_{is} = (k_{ha}^S[\mathrm{RI}]/k_{is})$ according to ref 8, or, more properly, $f_{is} = k_{ha}^{se}/k_{is}$ from our kinetics treatment. It is, perhaps, not surprising that for A/RI the $T_1 \rightarrow S_0$ radiative process, which was involved in Kasha's discovery of the external heavy-atom effect,[2] has the largest sensitivity factor, $f_p \simeq 1.5 \times 10^3$. The significantly smaller enhancement of radiationless $T_1 \rightarrow S_0$ decay, $f_{nr} \simeq 2.0 \times 10^2$, is in agreement with observations of enhanced phosphorescence in H-A solvents.[21,31] Interpretation of our estimated limiting value for $f_{is} \leq 6.8 \times 10^2$ is less straightforward because the rate of $S_1 \rightarrow T$ intersystem crossing depends on the relative energies of S_1 and the nearly isoenergetic higher triplet T. The energy difference between S_1 and T is known to be strongly influenced by solvent changes and, at least with some meso-substituted anthracenes, such solvent effect can defeat the functioning of H-A induced $S_1 \rightarrow T$ crossing.[21,39,40]

We have demonstrated that competitive deactivations of $^3A^*$ by ^{1}A and MeI in benzene and by EtI and Fe in methylcyclohexane are linearly independent events, not requiring the postulation of necessary triplet excimer or exciplex intermediates.

For the first time we have established the enhancement of the efficiency of TTA in anthracene by interaction with MeI at very high concentration (≥2 M) and have proposed interaction with quintet encounter pairs as the source of this effect.

Experimental Section

Materials. Anthracene (Eastman, blue violet fluorescent) was recrystallized from cyclohexane, chromatographed on Alumina with *n*-hexane as eluent, and recrystallized two more times, mp 217–218 °C. **Ferrocene** (Matheson, Coleman and Bell) was recrystallized thrice from ethanol and sublimed under reduced pressure, mp 175–176 °C. **Benzene** (Mallinkrodt reagent grade) was purified by the Metts exhaustive photochlorination procedure.[10] **Methylcyclohexane** (Baker, Photrex reagent) was used as received. **Methyl iodide** (Aldrich, 99%), if colorless, was refluxed with granular or mossy zinc for 1 h and distilled in the dark, bp 43–44 °C. If yellow in color, MeI was triply distilled over mossy zinc, purity >99.7%, GLC. **Ethyl iodide** (Mallinkrodt analytical reagent), always received dark pink in color, was purified by successive three or four distillations over mossy or granular zinc in the dark, bp 72.0–73.0 °C, purity >99.7%, GLC. Both MeI and EtI were either used immediately following purification or stored in degassed ampules in the dark at −20 °C for later use. MeI and EtI were allowed to reach room temperature before use since their concentrations were often based on

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(43) This analysis ignores the multiplicities of the paired states and does not preclude the possibility that paired states of a specific multiplicity are much shorter lived than this effective lifetime.

(44) (a) McVey, J. K.; Shold, D. M.; Yang, N. C. *J. Chem. Phys.* **1976**, *65*, 3375. (b) Cohen, M. D.; Ludmer, A.; Yakhot, V. *Chem. Phys. Lett.* **1976**, *38*, 398.

their volume and density. All handling of RI samples was in the dark or in very diffuse light.

Degassing of Solutions. Known volumes of neat MeI or EtI or Fe solutions of appropriate concentrations were syringed into sidearms equipped with break seals and degassed by 11–14 freeze–pump–thaw cycles to stick vacuum ($<10^{-5}$ (mmHg)).[45] Degassed sidearms wrapped with aluminum foil were connected to the main body of the flash cell which included the cylindrical flash cell (l = 15.0 cm) fitted at the ends with Pyrex flats, a degassing bulb, and a calibrated UV cell for monitoring the anthracene concentrations of degassed solutions. The flash cell system was then cleaned by rinsing several times with distilled acetone, drying under reduced pressure, rinsing with the solvent employed in the experiment, and repeating the drying procedure. Exactly 40 mL of anthracene solution was syringed into the degassing bulb which contained a stainless steel bullet for breaking the break seal(s). Benzene solutions required at least 11 freeze–pump–thaw cycles for thorough degassing while methylcyclohexane solutions required 12–13 cycles.

Transient Measurements. The flash spectroscopy apparatus was that previously described.[10,11] A 6-nm band-pass at $^1/_2$ intensity was employed on the monochromator.[10] The light of the two air-discharge flash lamps was filtered with a solution (13.5 g of $CuSO_4 \cdot 5H_2O$, 27.5 mL of NH_4OH to 250 mL with H_2O, 1 cm path length) having <1% transmittance at $\lambda < 373$ nm and maximum transmittance at 424 nm for all runs except 1j, 1k, 2a, 2b, and 2c for which a more dilute filter solution was employed having <1% transmittance at $\lambda < 358$ nm. The monitoring beam was filtered through a 1 cm path length solution (27.1 g of $CuSO_4 \cdot 5H_2O$, 30.2 g of $NaNO_2$, and 50 mL of NH_4OH to 1 L with H_2O) having 1% transmittance at $\lambda < 400$ nm, except for runs 1j, 1k, 2a, 2b, and 2c for which a more dilute filter solution was employed which transmitted light of $\lambda > 346$ nm. The transient signals were monitored at 429 nm for benzene and at 421 nm for methylcyclohexane solutions. After 2–4 $^3A^*$ decay curves were recorded, a portion of the solution was transferred to the UV sidearm and the UV absorbance obtained (Perkin-Elmer λ5). The break seal was then broken, uniform solution was attained by shaking, and the procedure was repeated. In the Fe/EtI experiment the Fe sidearm break seal was always broken first. With RI, data were collected within the first 10 flashes for extrapolation to the $k_{1,0}'$ values.

Concentrations. Anthracene concentrations were based on absorbances in the side cells with use of the following molar absorptivities (λ, nm; ϵ, M^{-1} cm^{-1}): (378.6; 7.94×10^3), (359.1; 8.49×10^3), (368.2; 2.16×10^3), (349.2; 3.10×10^3) in benzene, and (375.6; 8.42×10^3), (356.4; 8.65×10^3) in methylcyclohexane. Small corrections for the absorbance of MeI and EtI were applied (λ; ϵ): (378.6; 1×10^{-3}), (368.2; 5×10^{-3}), (359.2; 1.7×10^{-2}) for MeI in benzene, and (375.5; 4×10^{-3}), (356.4; 4×10^{-2}) for EtI in methylcyclohexane. Fe (2×10^{-7} M) does not contribute at the monitoring λ's. No changes in the ϵ values of A were noted in the presence of 1.08 M MeI in benzene.

Concentrations of MeI and EtI were determined by GLC with use of EtI as internal standard for MeI and vice versa. A DB-5 fused silica capillary column (30 m × 0.32 mm OD) was employed in a Varian-Aerograph Model 2700 instrument and a Hewlett Packard 3390A electronic integrator. Concentrations determined in this way checked closely with those expected from RI volumes and densities.[46]

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(45) Initial experiments in which MeI and EtI in benzene and methylcyclohexane solutions were degassed in the sidearms generally gave higher apparent quenching constants.

(46) **Note Added in Proof:** The analysis of k_2 has recently been refined[47] to account for two nearly cancelling errors: (a) the model reaction on which k_{dif} was based is an A + B reaction for which $k_{obsd} \simeq (1/2)k_{dif}^{AB}$; (b) TTA is an A + A reaction for which $k_a = k_{dif}^{AA} = (1/2)k_{dif}^{AB}$. This refinement does not significantly affect the conclusions in this paper.

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Spectroscopic Studies of the Binuclear Ferrous Active Site of Deoxyhemerythrin: Coordination Number and Probable Bridging Ligands for the Native and Ligand Bound Forms

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Abstract: The binuclear Fe(II) active site of deoxyhemerythrin (deoxyHr) was studied using absorbance, circular dichroism (CD), variable-temperature magnetic circular dichroism (MCD), and EPR spectroscopies. CD studies show the native deoxyHr site contains one five-coordinate and one six-coordinate ferrous iron. In addition N_3^-, OCN^-, and F^- were found to bind to the active site, producing large spectral changes best explained as the binding of a single anion to the five-coordinate iron, yielding two six-coordinate Fe(II)s. No other anions were found to bind. The variable-temperature MCD data were interpreted by fitting the data to energies and g values of low-lying binuclear ferrous ground states, predicted by calculations employing the spin Hamiltonian containing both exchange coupling ($\mathcal{H} = -2JS_1 \cdot S_2$) and single-site zero field splitting (ZFS). The native deoxyHr data showed the Fe(II) to be antiferromagnetically coupled with $-J \sim 12\text{–}38$ cm^{-1}, which indicates the irons are likely bridged by hydroxide. The ligand bound forms all show weak ferromagnetic coupling, indicating the OH superexchange pathway is perturbed significantly. The binding of anions apparently changes the charge density of the iron, raising the pK_a of the bridge, and likely results in protonation of the hydroxide. Further, the intensity mechanism of an interesting $g_\parallel \sim 16$ EPR signal originating from the $|4,\pm4\rangle$ ground state in the deoxyN_3^-Hr species is analyzed. Finally, these results on exogenous ligand binding and endogenous ligand bridging at the binuclear Fe(II) site of Hr are correlated to the protein reactivity.

Hemerythrin (Hr) is a binuclear, non-heme iron protein, which serves as the oxygen-carrying protein in four phyla of marine organisms.[1] Most of these are octameric and bind dioxygen noncooperatively, although the Hrs from at least some brachiopods[2] do bind dioxygen cooperatively. Hemerythrin exists in two physiologically important forms: oxyhemerythrin, having two ferric irons with peroxide bound end-on to only one iron, and

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