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Quenching of Singlet Excited States of Electron-Deficient Anthracenes by Allyl- and Benzyltrialkylstannanes[†]

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Abstract: Allyl- and benzyltrialkylstannanes quench the fluorescent singlet states of several meso-substituted anthracenes. Intermediacy of a charge-stabilized exciplex is supported by correlation of fluorescence quenching rate constants with anthracene reduction potential for the constant quencher benzyltrimethylstannane and with the ionization potential of the quencher stannane for the constant fluorescor 9,10-dicyanoanthracene (DCA). Quenching of DCA by a series of para-substituted (X = Cl, F, H, CH_3, OCH_3) benzyltri-*n*-butylstannanes can be analyzed by a Hammett treatment ($\rho = -1.4$ vs. σ_p). Quantum yield measurements of DCA disappearance as a function of both the nature of X and the quencher concentration provide rate constants for product-forming channels during exciplex decay. Limiting quantum yields for product formation are shown to increase with increasing electron-withdrawing nature of X while the rate constant for product formation is nearly invariant with X. Rate constants for radiationless return to unchanged ground states increase dramatically as X becomes electron releasing. A rationale for all observed data in terms of reversible exciplex formation and subsequent decay is presented.

Bimolecular photophysical interactions between donor–acceptor (D–A) pairs, mediated by excited state complex (exciplex) formation, have proved to be pervasive. Charge-transfer (CT) stabilization has been shown to be important during deactivation of electron-deficient excited states (A*) with such diverse ground-state donors as amines,[1] phosphines,[2] thiols,[3] and sulfides[4] and electron-rich aromatics,[5] dienes,[6] olefins,[7] and hydrocarbons.[8] In many cases, clear correlations between donor oxidation or ionization potential and rate constants for overall deactivation of A* have been obtained and cited as evidence in favor of intervention of CT-stabilized exciplexes. In other instances, ion radical intermediates have been directly observed spectroscopically. Few systems, however, have provided direct chemical (product) evidence in favor of full electron transfer during exciplex decay.

Group 4A organometallics, particularly those containing M–C σ bonds β to a neighboring π system, have been shown to be exceedingly electron rich. Photoelectron spectroscopic studies[9] indicate that ionization potentials can be in the range typical of conventional donors effective in CT exciplex schemes, and many such organometallics readily form ground-state CT complexes with electron-deficient acceptors such as TCNE.[10] In ground-state chemistry, the facile reactions of organosilicon, -tin, -germanium, and -lead species with electrophiles have been elegantly shown to proceed by way of charge-transfer intermediates.[11]

This paper presents details of a study of the deactivation of electron-deficient excited singlet states, particularly 9,10-dicyanoanthracene (DCA), by allylic and benzylic organostannanes. Steady-state analysis of fluorescence quenching and photochemical product formation as a function of quencher concentration allows nearly complete dissection of the exciplex-mediated decay kinetics of these systems and reveals several unusual facets of the processes which occur.[12]

Results

Fluorescence Quenching. Rate constants (k_q^f) for overall fluorescence quenching of singlet DCA* in benzene by the lifetime method are listed in Table I for a variety of organotins. Also listed in Table I are gas phase vertical ionization potential data for the various quenchers; adiabatic values are uniformly about 0.4 eV lower.[10]

Table I. Rate Constants for Quenching of 9,10-Dicyanoanthracene Fluorescence by Organotin Compounds

compd	k_q^f (M^{-1} s^{-1}, $\times 10^{-9}$)[a]	I_p^v (eV)[b]
Me_4Sn	0.07	9.8
$PhCH_2SnPh_3$	4.3	8.4
$PhCH_2Sn(n\text{-}Bu)_3$	7.9	7.9
$PhCH_2SnMe_3$	10.1	8.1
allyl$SnMe_3$	5.1	8.5
allyl$Sn(n\text{-}Bu)_3$	4.1	

[a] In benzene by lifetime method. [b] Vertical ionization potential.

Table II. Rate Constants for Quenching of 9,10-Dicyanoanthracene Fluorescence by Para-Substituted Benzyltri-*n*-butylstannanes, $p\text{-}XC_6H_4CH_2Sn(n\text{-}C_4H_9)_3$

X	k_q^f (M^{-1} s^{-1}, $\times 10^{-9}$)[a]	X	k_q^f (M^{-1} s^{-1}, $\times 10^{-9}$)[a]
Cl	3.8	CH_3	10
F	5.9	CH_3O	21
H	7.9		

[a] In benzene by lifetime method.

Generally, k_q^f is seen to depend inversely on ionization potential. Thus the following trend (compound, k_q^f, IP): $PhCH_2SnMe_3$, 10.1 × 10^9 M^{-1} s^{-1}, 8.1 eV > $PhCH_2SnPh_3$, 4.3 × 10^9 M^{-1} s^{-1}, 8.5 eV ~ allyl$SnMe_3$, 5.1 × 10^9 M^{-1} s^{-1}, 8.5 eV > Me_4Sn, 7 × 10^7 M^{-1} s^{-1}, 9.8 eV. Steric effects counter the effect of increased ease of ionization, however, in both the benzyl and allyl series: $PhCH_2SnMe_3$, 10.1 × 10^9 M^{-1} s^{-1}, 8.1 eV > $PhCH_2Sn(n\text{-}Bu)_3$,

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[†] This paper is dedicated to George S. Hammond on the occasion of his 60th birthday.

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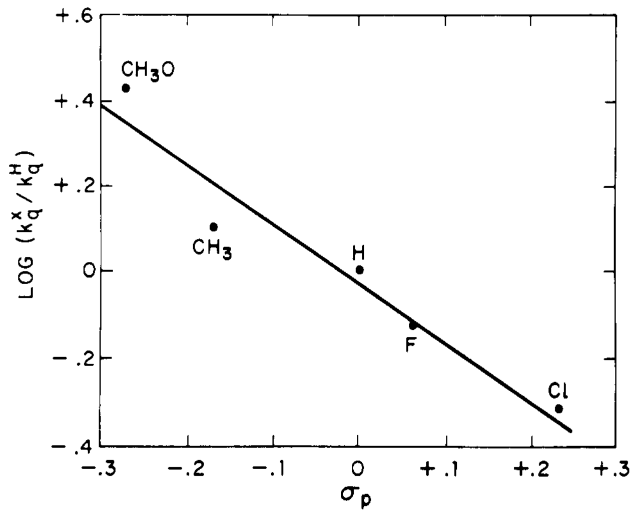

Figure 1. Plot of log (k_q^X/k_q^H) vs. σ_p for the fluorescence quenching of DCA* by p-$XC_6H_4CH_2Sn(n\text{-}Bu)_3$ in benzene.

Table III. Rate Constants for Quenching of Substituted Anthracene Fluorescence by Benzyltrimethylstannane

anthracene	$E_{1/2}{}^{*a}$	$k_q{}^f$ (M^{-1} s^{-1}, $\times 10^{-9}$)^b
9,10-dicyano	2.57	7.69
9-cyano	2.18	0.146
9,10-dibromo	2.17	0.339
9,10-dichloro	1.95	0.027
anthracene	1.78	0.006^c
9-methyl	1.69	<0.009^d
9,10-dimethyl	1.57	<0.002^d

[a] $E_{1/2}{}^* = E_{1/2}{}^0 + {}'E_{0,0}$, taken from Weiss,[2] in eV. [b] In toluene by intensity method. [c] ±0.001. Quencher concentrations up to 1.5 M were used ($I_0/I = 1.045$). [d] Upper limit, no quenching observed with $[Q]_{max}$ of 0.10 M (9-methyl), and 0.5 M (9,10-dimethyl).

7.9×10^9 M^{-1} s^{-1}, 7.9 eV and allylSnMe$_3$, 5.1×10^9 M^{-1} s^{-1}, 8.5 eV > allylSn(n-Bu)$_3$, 4.1×10^9 M^{-1} s^{-1}. The special nature of the β-unsaturated organotin function must be noted. Toluene ($I_p{}^v$ = 8.8 eV) is not an effective quencher of 9,10-DCA singlets ($\Upsilon_s{}^{toluene} = \Upsilon_s{}^{benzene}$, $k_q < 1 \times 10^6$ M^{-1} s^{-1}), but organometal substitution at the benzyl center renders the compound effective.

Heavy-atom-induced intersystem crossing has been shown by Vander Donckt[13] to account for the quenching by Me$_4$Sn (7×10^7 M^{-1} s^{-1}, 9.8 eV) and we attribute approximately 1% of the observed quenching in the benzyl and allyltin series to this mechanism.

Table II lists observed fluorescence quenching rate constants for 9,10-DCA by a series of para-substituted benzyltri-n-butylstannanes. Rates are seen to increase as the electron-releasing ability of substituent X increases. A plot of log (k_q^X/k_q^H) vs. σ_p is linear with slope −1.4, Figure 1.

Table III presents measured rate constants for quenching of several meso-substituted anthracenes by the constant quencher benzyltrimethylstannane. Quenching efficiency is found to fall off rapidly as the oxidizing power of the fluoror excited state, as measured by the sum of the ground-state reduction potential ($-E_{1/2}$ vs. Hg in CH$_3$CN)[2] and the singlet excitation energy (${}^1E_{0,0}$), decreases.[14] By taking the diffusion rate in toluene to be k_{dif} = 1.12×10^{10} M^{-1} s^{-1} and adopting the Evans method[15] of evaluating charge-transfer components to quenching, a plot of log [$k_q{}^f$(k_{dif} − $k_q{}^f$)] vs. $E_{1/2}{}^*$ was found to be linear with a slope of 4.83 (eV)$^{-1}$ and intercept −12.12 (correlation 0.988), Figure 2.

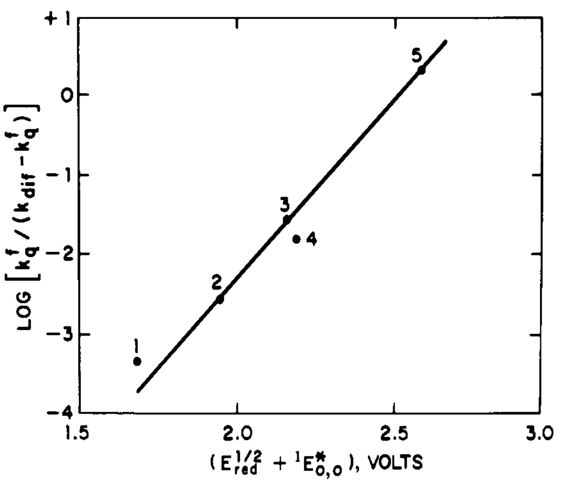

Figure 2. Plot of log {$k_q{}^f$/(k_{dif} − $k_q{}^f$)} vs. $E_{1/2}{}^*$ for benzyltrimethylstannane quenching substituted anthracene fluorescence in toluene. $E_{1/2}{}^*$ values from ref 2. Data points: (1) anthracene; (2) 9,10-dichloroanthracene; (3) 9,10-dibromoanthracene; (4) 9-cyanoanthracene; (5) 9,10-dicyanoanthracene.

Table IV. Effect of Solvent Polarity on Quenching of Anthracenes by Benzylstannanes

solvent	$E_T{}^a$	ϵ^b	$k_{dif}{}^c$	$k_q{}^f$-(DCA)^d	$k_q{}^f$-(DClA)^e
CH_3CH_2OH	51.9	24.6	6.03	8.16	1.82
CH_3CN	46.0	37.5	18.8	17.6	f
THF	37.4	7.58	11.8	11.0	1.42
C_6H_6	34.5	2.28	11.1	8.7	0.071
$CH_3C_6H_5$	33.2	2.38	9.97	7.5	0.080
c-C_6H_{12}	31.2	2.02	6.31	10.6	0.036
n-C_6H_{14}	30.9	1.88	20.7	17.4	

[a] Kosower's E_T parameter, from Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker, Inc.: New York, 1966; pp 85–7. [b] Dielectric constant, from Murov (op. ct., footnote a). [c] Diffusion limit in units of 10^9 M^{-1} s^{-1}. [d] Quenching of 9,10-dicyanoanthracene by benzyltrimethylstannane; units 10^9 M^{-1} s^{-1}; intensity method. [e] Quenching of 9,10-dichloroanthracene by benzyltri-n-butylstannane; units 10^9 M^{-1} s^{-1}; intensity method. [f] Tin compound only partially soluble in this solvent.

The effect of solvent polarity on the quenching of 9,10-DCA singlets by benzyltrimethylstannane was examined and results are given in Table IV. Observed $k_q{}^f$ values are near the diffusion-control limits in all solvents examined for this system. A similar but more limited series of solvents was employed for quenching of 9,10-dichloroanthracene by benzyltri-n-butylstannane (Table IV). Here $k_q{}^f$ increased as solvent polarity increased.

Product Formation. During the course of irradiation of 9,10-DCA solutions in benzene, photobleaching of the anthracene chromophore was observed in the presence of added benzylstannanes. A preparative photolysis (see Experimental Section) of 9,10-DCA and PhCH$_2$Sn(n-Bu)$_3$, using a Pyrex filter, afforded products attributed to over-irradiation. We postulate the initial formation of a 9,10-dihydroadduct (e.g., I, Scheme I) which suffers predominant secondary homolysis at the tin–doubly benzylic site rather than at the alternative benzyl–benzyl position. Subsequent rearomatization (loss of ·CN; undetected) gives the observed products.

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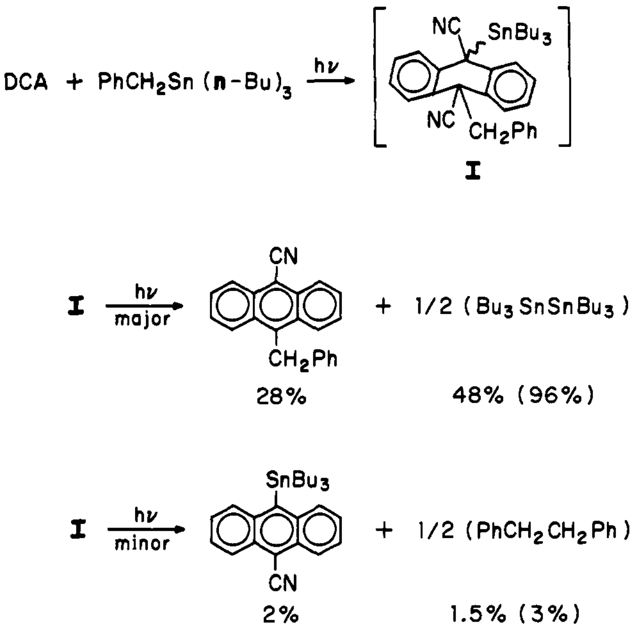
Scheme I



Under analytical conditions (uranium glass filter), clean photobleaching of 9,10-DCA can be observed to 80% disappearance. Quantum yields of chromophore loss (ϕ_p) have been determined for the series of quenchers p-$XC_6H_4CH_2Sn(n\text{-}Bu)_3$ (X = Cl, F, H, CH_3, OCH_3) as a function of quencher concentration, [Q]. From a plot of $(\phi_p)^{-1}$ vs. $[Q]^{-1}$ one obtains a family of straight lines of nearly equal slope, the intercepts of which (α; $\alpha^{-1} = \phi_p^{\text{limit}}$ at $[Q] = \infty$) depend on the nature of substituent X (Figure 3).

Discussion

The quenching of meso-substituted anthracene fluorescence by allyl- and benzylstannanes is proposed to occur via a charge-transfer-stabilized exciplex-mediated bimolecular reaction mechanism. Detailed asspects of the proposed scheme will be presented and supported below. Initially, however, it is necessary to delineate several key observations which support the general scheme and eliminate trivial mechanisms.

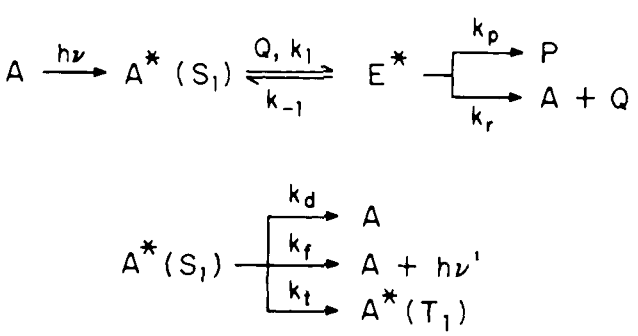
Ground-state charge-transfer complexes were not observed for any anthracene derivative in the presence of any of the organotin compounds used in this work in any solvent. Further, the visible region fine structures of the lowest singlet–singlet transitions of 9,10-DCA are not perturbed, within the accuracy of our measurements, by the presence of up to 2.0 M stannane. (CT complexes are observed, transiently, between organostannanes and more potent acceptors, e.g., TCNE,[10] quinones.[16])

Excitation spectra of the fluorescent anthracenes are also unaffected by the presence of organotins. No exciplex emission was observed, however, in any system examined.

The ultraviolet spectra of benzylstannanes extend to ca. 310 nm ($\epsilon \sim 100$) in polar and nonpolar solvents. Thus exothermic singlet energy transfer from excited anthracenes to the organotins is not feasible. Although the triplet energies of organotin compounds are unknown, we do not anticipate an unusually large S–T splitting in these systems. Conversely, anthracene triplets reside near 45–55 kcal/mol, so we therefore feel confident that triplet energy transfer cannot account for the chemistry we report.

The fluorescence quenching data given in Tables I–III indicate that quenching efficiency tends to increase as the ease of ionization of the organometal increases or as the oxidizing power of the fluoror increases. These data all support a charge-transfer-stabilized quenching event in which the electropositive organometal acts as an electron donor. We therefore adopt the overall quenching scheme depicted in Scheme II as descriptive. In the scheme the terms and rate constants have their usual meaning: the excited singlet $A^*(S_1)$ of anthracene A can fluoresce (k_f); decay radiationlessly (k_d), intersystem cross (k_t), or interact bimolecularly with stannane quencher Q in an encounter limited bimolecular event ($k_1 \lesssim k_{dif}$), which may be reversible (k_{-1}), to form an exciplex (E^*). E^* can form product (k_p) or decay (k_r) to A and Q ground states. We now proceed to support the proposed mechanism in detail and to provide some insight into the electronic factors which govern the decay of E^*.

Scheme II



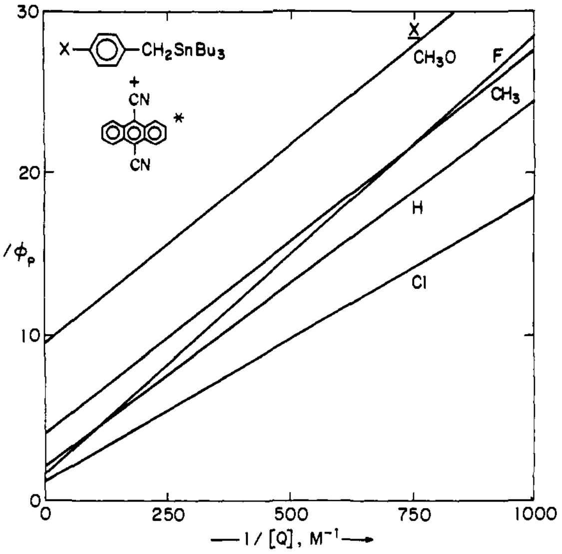


Figure 3. Plot of ϕ_p^{-1} vs. $[Q]^{-1}$ for DCA* quenching by p-$XC_6H_4CH_2Sn(n\text{-}Bu)_3$ in benzene.

Overall Fluorescence Quenching. The overall fluorescence quenching rate constant k_q^f obtained from a Stern–Volmer treatment (Tables I–IV) is a composite rate constant (eq 1) which reflects exciplex formation, reversion, and subsequent decay via both product forming and non-product forming channels.

$$k_q^f = k_q^p + k_q^r = \frac{k_1(k_p + k_r)}{k_{-1} + k_p + k_r} \qquad (1)$$

For the series of para-substituted benzylstannanes the Hammett plot (Figure 1), relating overall fluorescence quenching to the electron releasing ability of substituent X, has slope −1.4 vs. σ_p. This slope is consistent with rate-determining electron transfer during exciplex formation from ground-state quencher stannane to excited singlet A* (eq 2). The Hammett slope (−1.4) implicates

$$p\text{-XPhCH}_2\text{SnBu}_3 + \text{A}^* \longrightarrow \left[p\text{-XPh}\overset{\cdot +}{\text{CH}_2}\text{SnBu}_3/\text{A}^{\cdot -}\right]^* \qquad (2)$$

a degree of positive charge buildup at the benzylic carbon during the exciplex formation. The magnitude of the ρ slope does not indicate a large degree of electron demand at the benzylic center, however. The ρ value is similar to that observed during free-radical bromination (Br_2, $h\nu$, or N-bromosuccinimide) of para-substituted toluenes.[17] We also note that the correlation we obtain employs

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[16] Kochi, J. K.; Chen, K. S.; Wan, J. K. S. *Chem. Phys. Lett.* **1980**, *73*, 557.

Table V. Dissection of Exciplex Decay Rate Constants for DCA* Quenching by p-XPhCH$_2$SnBu$_3$[a]

X	k_q^f	α	$(k_1 k_p)/(k_{-1} + k_r + k_p)$	$k_q^p = \alpha k_q^f$	$k_q^r = (1-\alpha)k_q^f$
Cl	3.8	0.91 ± 0.08	3.5 ± 0.5	3.5 ± 0.3	0.3 ± 0.3
F	5.9	0.55 ± 0.05	2.5 ± 0.4	3.2 ± 0.3	3.1 ± 0.3
H	7.9	0.45 ± 0.04	2.8 ± 0.5	3.5 ± 0.4	4.8 ± 1
CH$_3$	10	0.25 ± 0.03	3.1 ± 0.4	2.5 ± 0.3	7.5 ± 1
CH$_3$O	21	0.11 ± 0.01	2.7 ± 0.5	2.1 ± 0.2	18 ± 1

[a] All rate constants in 10^9 M^{-1} s^{-1}.

Table VI. Estimate of Exciplex Reversion Component by the Method of Evans[a]

X	$(k_r + k_p)/k_{-1}$	k_p/k_{-1}
Cl	0.61	0.55
F	1.4	0.79
H	3.8	1.7
CH$_3$	ind[b]	ind[b]
CH$_3$O	ind[b]	ind[b]

[a] Derived from parameters in Table V assuming $k_1 = k_{dif}$. [b] For these substituents $k_q^f \sim k_{dif}$ so that application of the method becomes indeterminant.

σ_p values, rather than σ_p^+, to accommodate the k_q^f value when X = F.

Dissection of Radiationless Processes. From the plots of $(\phi_p)^{-1}$ vs. $[Q]^{-1}$ shown in Figure 3 we can obtain the following parameters: α, the inverse of the intercept, is the limiting quantum yield for product formation; and k_q^p, the slope, is the rate constant for exciplex decay to products (eq 3) of Scheme II. Since the overall

$$k_q^p = k_1 k_p / (k_{-1} + k_p + k_r) \qquad (3)$$

observed fluorescence quenching rate constant, k_q^f, equals the sum of the product forming rate constant (k_q^p) and the radiationless rate (k_q^r), we obtain k_q^r from k_q^f (Table II) and k_q^p, the slopes of Figure 3. Since $\alpha = \phi_p^{limit}$, αk_q^f also is a measure of k_q^p, obtained independently of the value derived from Figure 3. These parameters are collected in Table V. The agreement between k_q^p values obtained by the two procedures described above argues for the validity of the methods used.

Several important conclusions can be drawn from the data in Table V. First, the product-forming rate constants k_q^p remain roughly constant independent of the nature of substituent X. This constancy is maintained despite the substantial dependence of the limiting quantum yield, α, on X. Second, the substituent X effects the radiationless decay of the exciplex, leading to unchanged substrates A and Q, dramatically and systematically. As X becomes more electron releasing, k_q^r increases substantially; on substituting CH$_3$O for Cl, k_q^r increases by a factor of 60.

If it is assumed that exciplex formation is diffusion controlled (Evans method),[15] $k_1 = k_{dif}$, then $k_q^f/(k_{dif} - k_q^f) = (k_r + k_p)/k_{-1}$ and $\alpha(k_r + k_p)/k_{-1} = k_p/k_{-1}$. If this technique is adopted, then the values in Table VI are obtained. These data indicate that exciplex reversibility strongly depends on the nature of substituent X. Exciplex reversion becomes increasingly unlikely as X becomes more electron donating, while exciplex decay via radiationless channels (k_r or k_p) becomes more probable. In the absence of ionization potential data explicitly correlating the electron donor power of X with increased ease of ionization of the benzylstannanes in this series we cannot be certain of the electronic origin of this effect, but we suspect that the exciplex lifetime probably increases as the donor power of X increases.

Other studies have determined that, within a homologous series, the stronger the exciplex binding, the faster the nonradiative decay rates become. Mataga[18] has explained this effect as a competition between ionic dissociation and decay to the ground state. We suspect a similar phenomenon in the present case.

Thermodynamics of Electron Transfer in the Exciplex. The one-electron oxidation of organotin compounds by ground-state electron acceptors is well established.[10,11] Carbon–tin bond scission is often observed during such processes. We have attempted to probe the likelihood of electron transfer in the exciplexes proposed in the present system by two methods.

Solvent effects on exciplex emission spectra and other properties have been used to ascertain the dipole moments of exciplexes. We examined the effect of solvent variations on overall fluorescence quenching rate constants for the system 9,10-DCA/PhCH$_2$SnMe$_3$ (Table IV) and observed that $k_q^f \sim k_{dif}$ for all solvents examined ($50 < E_T < 30$ kcal/mol). We infer from this result that ΔG for electron transfer is exothermic for this system in all solvents. This result provides no measure of the degree of electron transfer that occurs in the exciplex, but it does suggest that full electron transfer is energetically feasible.

In order to more fully assess the effect of solvent polarity on quenching rates, we examined quenching of the less electron poor anthracene 9,10-dichloroanthracene (9,10-DClA) by benzyltri-n-butylstannane in order to extend the range of observed k_q^f values. Results listed in Table IV indicate that k_q^f increases with increasing solvent polarity (E_T or ϵ) for this system and that rate constants are below k_{dif} in all solvents. No clear functional relation was found between any of k_q^f, k_q^f/k_{dif}, or $k_q^f/(k_{dif} - k_q^f)$ and either E_T or ϵ. However, the ratio of k_q^f/k_{dif} increased from 5.7×10^{-3} (cyclohexane) to 0.3 (ethanol) indicative of the importance of a high degree of CT during quenching.

In another series of experiments we determined k_q^f values in toluene for PhCH$_2$SnMe$_3$ quenching a variety of substituted anthracenes (Table III). According to the treatments of Cohen[14a] and Wagner,[14b] derivable from the work of Weller,[14c] the slope of the log k_q^f (or log $[k_q^f/(k_{dif} - k_q^f)]$ in the Evans formalism[15]) vs. $E_{1/2}$* plot is related to the thermodynamics of the electron-transfer process during exciplex formation. The observed slope in the present system, 4.83 (eV)$^{-1}$, represents roughly 30% of the maximum theoretical slope, 16.84 (eV)$^{-1}$. This value can be compared to those observed in diverse systems: ~8–12% for ketone triplets in cycloaddition reactions,[19] ~30% for the 1-cyanonaphthalene–naphthalene exciplex in nonpolar solvents,[20] and 40% for toluene quenching of α-trifluoroacetophenone triplets.[21]

The interpretation of the observed slope in this and other systems is ambiguous. In fact the meaning of such plots has been questioned.[21-23] The interpretation in the present case is complicated by the irreversibility of the benzyltin oxidation, so that meaningful thermodynamic parameters are unavailable. This situation has been addressed by Scandola, Balzani, and Schuster,[23] who note that the slopes of log k vs. ΔG plots in such systems are usually in the range of 20–50% of the theoretical maximum. Slopes less than 100% of the maximum are, however, compatible with full electron transfer during the quenching event, but they do not demand it.

For the DCA/PhCH$_2$SnMe$_3$ system, the absence of solvent effect on k_q^f (near k_{dif}), coupled with the free-energy relation observed (Figure 2) for a series of substituted anthracene fluorors, may implicate full electron transfer during quenching. At the least it places this system in the region of $\Delta G \lesssim 0$ for the thermodynamics of electron transfer. Since the ΔG region probed experimentally is 0.79 V (18 kcal/mol) and the log k_q^f variation in this region is over three orders of magnitude, the treatment of

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Scandola et al.[23] suggests that in fact ΔG is negative but that the standard activation free energy to electron transfer (or to electron transfer followed by subsequent bond breaking in this thermodynamically irreversible oxidation), $\Delta G^{\ddagger}(0)$, is positive and in the range 6–10 kcal/mol. By this analysis, k_p, the bond cleavage rate constant is, as a lower limit, in the range 10^6–10^8 s^{-1}. This rate constant is thus competitive with other unimolecular exciplex decay processes and suggests that product formation occurs as a direct result of electron transfer and subsequent bond breaking during the quenching event.

Mechanism of Product Formation. The final products obtained during photolysis of 9,10-DCA–benzyltri-*n*-butylstannane mixtures are proposed to arise via secondary photolysis of a 9,10-adduct (I, Scheme I). The intermediacy of a species such as I is supported by the clean kinetic photobleaching observed as well as the nature and yields of the final products. We envision formation of I as being a direct consequence of the CT character of the exciplex intermediate: charge transfer from the σ–π delocalized HOMO[10] of the benzylstannane substantially weakens the C_{benzyl}–Sn bond. Facile bond cleavage to ion/radical pairs[10d] within the exciplex cage, and subsequent collapse to I, is proposed to occur in competition with radiationless exciplex decay by nonproduct-forming channels. The more efficient formation of products ($\phi_p^{limit} = \alpha$, Table V) when substituent X in p-$XPhCH_2Sn(n\text{-}Bu)_3$ is electron withdrawing is thought to be a consequence of the internal competition between exciplex reversion (k_{-1}), which is rapid when X is electron withdrawing, and decay via nonproduct-forming channels (k_r). As the electron donor power of substituents X increase, k_{-1} decreases (exciplex lifetime increases), but k_r increases dramatically, so that ϕ_p^{limit} decreases. Thus the rate constants for various decay processes of E* (k_{-1}, k_p, k_r) are determined to be intimately related to the electronic nature of the exciplex.

Conclusions

Excited singlet states of electron-deficient anthracenes are quenched by benzyl- and allyltrialkylstannanes via a charge-stabilized exciplex. In the case of benzylstannanes, the degree of electron transfer is found to be approximately 30% in nonpolar solvents. Quenching rate constants correlate with parameters related to the ease of ionization of the benzyltin quencher and the excited state reduction potential of the anthracene acceptor. Exciplex decay to products occurs with an unvarying rate constant within the homologous series *p*-$XPhCH_2SnBu_3$/9,10-DCA, but nonradiative exciplex rates vary by a factor of 60, increasing as the exciplex reversion rate decreases and as the exciplex lifetime increases. Product formation occurs as a consequence of C_{benzyl}–Sn bond weakening in the CT-stabilized exciplex.

Experimental Section

Materials. All anthracenes used in this work were commercial samples recrystallized and/or sublimed before use. UV–vis spectra and fluorescence lifetimes agreed with those in the literature.

Organostannanes were prepared by Grignard methods from trialkyltin halides and the appropriate alkyl, allyl, or benzyl halide and were distilled before use. The following are known compounds: tetramethyltin (Alfa), bp 78 °C; allyltrimethyltin, bp 55 °C (56 mm) (lit.[24] bp 128 °C (760 mm)); benzyltrimethyltin, bp 70 °C (3.6 mm) (lit.[25] bp 89 °C (9 mm)); allyltri-*n*-butyltin, bp 83 °C (0.35 mm) (lit.[26] bp 89 °C (0.3 mm)); benzyltri-*n*-butyltin, bp 105 °C (0.2 mm) (lit.[27] bp 192 °C (2.4 mm)); benzyltriphenyltin, mp 87–89 °C (ethanol) (lit.[28] mp 90 °C); all compounds exhibited satisfactory IR, NMR, and analytical data.

Para-substituted benzylstannanes, *p*-$XPhCH_2Sn(n\text{-}Bu)_3$, were prepared similarly. Physical properties follow. X = CH_3: bp 101–105 °C (0.1 torr); NMR ($CDCl_3/Me_4Si$) δ 7.0–6.6 (m, 4 H), 2.22 (2 singlets, 5 H), 1.5–0.6 (m, 27 H); C, H. X = F: bp 105–108 °C (0.5 torr); ^1H NMR δ 6.9–6.7 (m, 4 H), 2.26 (s, 2 H), 1.8–0.3 (m, 27 H); ^{19}F NMR ($CDCl_3$/F-11) δ −121.2; C, H, F. X = Cl: bp 117–120 °C (0.4 torr); NMR δ 7.1–6.7 (m, 4 H), 2.21 (s, 2 H), 1.8–0.6 (m, 27 H); C, H, Cl. X = OCH_3: bp 125–126 °C (0.1 torr); NMR δ 6.91–6.53 (m, 4 H), 3.68 (s, 3 H), 2.24 (s, 2 H), 1.6–0.5 (m, 27 H); C, H.

Methods. UV–vis spectra were obtained on a Cary 14 or Cary 219 spectrometer. Fluorescence spectra were obtained on a Perkin-Elmer MPF-3 fluorescence spectrophotometer. Entrance and exit slits were routinely 4 nm. All solvents were of spectrograde quality and used as received. Samples were run in 1 cm quartz cuvettes with and without nitrogen purging. Spectra were uncorrected. Lifetime measurements were made in a homemade phase-shift apparatus on air- and nitrogen-saturated samples. Concentrations of the fluorescent anthracenes were in the range 1×10^{-5}–1×10^{-4} M. Stern–Volmer plots were done with use of a minimum of four quencher concentrations. No curvature was noted in any system, and intercepts were 1.00 ± 0.02 in all cases. Slopes were determined by least squares, and correlation coefficients were always >0.997. Quenching rate constants were calculated from the slopes by using the measured lifetime of the fluoror.

Quantum yields were measured by using uranium glass filters (λ >410 nm) and ferrioxalate actinometry.[29] Solutions in benzene containing 9,10-dicyanoanthracene (OD at 426 nm ~3) and added tin compound ([Q] = 0.001–0.05 M) were photolyzed in a merry-go-round for various times. Aliquots were removed and diluted and the loss of 9,10-DCA determined spectrophotometrically, D_0 = od initial, D_t = od at time *t*. Plots of log (D_0/D_t) vs. *t* were linear to ca. 80% reaction. From the plots, pseudorate constants for DCA loss were obtained and quantum yields calculated from these and the light intensity. Values were reproducible to ±10%.

Isolation of Photoproducts. A benzene solution (1.0 L) of DCA (1.14 g, 5 mmol) and $PhCH_2SnBu_3$ (5.10 g, 20 mmol, 0.02 M) was irradiated, with continuous nitrogen sparging, with a Hanovia 450 W medium-pressure lamp through a Pyrex sleeve (λ >290 nm). The degree of fluorescence quenching under these conditions is roughly 55%. The mixture was irradiated for 4.75 h. After concentration, the residue was triturated with cold methanol and filtered to give 0.42 g (37%) of recovered DCA. The filtrate was concentrated and chromatographed (650 g activity I neutral alumina, 5.8 × 35 cm), eluting with $CHCl_3$/petroleum ether (5% $CHCl_3$ increasing to 50%) to give in order of elution: recovered benzylstannane (3.6 g, 70%), a mixed fraction (mixture A) of hexabutyldistannane and bibenzyl (1.60 g), and a second mixed fraction (mixture B) containing cyanoanthracenes. Mixture A was rechromatographed on silica gel with petroleum ethers to give hexabutyldistannane (1.41 g) and bibenzyl (.008 g). Mixture B was rechromatographed on silica to give 9-benzyl-10-cyanoanthracene (0.242 g, mp 148–151 °C, 163 °C after ethanol recrystallization; lit.[30] mp 166 °C), and 20 mg of an oily solid whose IR and NMR suggest the structure 9-cyano-10-(tri-*n*-butyl)stannylanthracene: IR (KBr) 2230 (CN); NMR ($CDCl_3/Me_4Si$) δ 8.4–8.2 and 7.8–7.5 (m, 8 H), 2.0–0.8 (m, 27 H). All known compounds exhibited appropriate physical and spectroscopic characteristics.

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