complexation (Table II). Isomerization via a common twisted intermediate (singlet or triplet) requires that $\Phi_{t\rightarrow c} + \Phi_{c\rightarrow t} = 1.0$,[3] as is the case in the presence, but not in the absence, of Lewis acids. Thus complexation serves to eliminate some energy wasting process. A singlet state mechanism has been proposed for the isomerization of ester **3** and cinnamic acid.[16] A small barrier to rotation might allow nonradiative decay to compete with bond rotation for singlet *trans*-**3** but not for *cis*-**3**. In support of this proposal we find that $\Phi_{t\rightarrow c}$ increases with increasing temperature, but $\Phi_{c\rightarrow t}$ does not. A decrease in the barrier to rotation upon Lewis acid complexation would thus be expected to increase $\Phi_{t\rightarrow c}$ but not $\Phi_{c\rightarrow t}$ as is experimentally observed. Other mechanisms for the effect of Lewis acids on isomerization quantum yields might also be envisioned (e.g., enhanced intersystem crossing, inversion of n,π^* and π,π^* state energies, sudden polarization, etc.).

As a preparative procedure, Lewis acid enhanced photoisomerization constitutes a substantial improvement in yield and convenience over previously published photochemical and nonphotochemical methods for the preparation of cis α,β-unsaturated esters.[17] In view of the importance of *cis*-crotonic and angelic acids as intermediates in organic synthesis,[18] we anticipate that this procedure will find widespread application. Preliminary results with α,β-unsaturated ketones and nitriles and with dienoic esters indicate that the scope of Lewis acid enhanced photoisomerization extends well beyond the examples here reported.[19]

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On the Formation of Aminyl vs. Aminoalkyl Radicals in the Photooxidation of Diethylamine†

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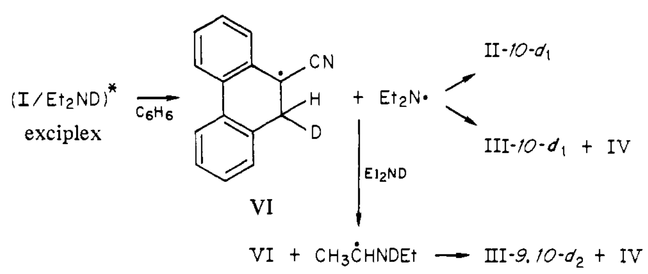
The abstraction of hydrogen atoms from amines in photochemical, free-radical, electrochemical, chemical, and enzymatic reactions continues to fascinate chemists.[2] One of the unsolved mysteries in this field is the reported ability of dialkylamines to form either dialkylaminyl or α-aminoalkyl radicals (eq 1).[3-9] In

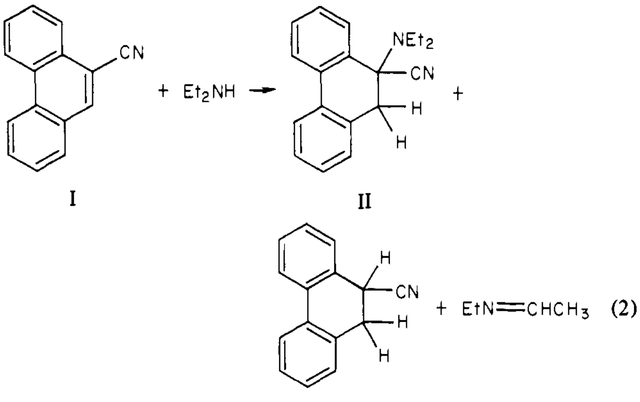
$$\mathrm{R_2CHNHR'} \xrightarrow{-\mathrm{H}\cdot} \mathrm{R_2CH\dot{N}R'} \text{ or } \mathrm{R_2\dot{C}NHR'} \qquad (1)$$

fact two recent reports from the same research institution present different conclusions as to which radical is formed upon reaction of *tert*-butoxy radicals with dialkylamines.[6,7] According to the most current thermochemical data, the α-C–H homolytic bond dissociation energy should be lower than the N–H energy for α-substituted dialkylamines (diethyl, diisopropyl, etc.) and similar to the N–H energy for dimethylamine.[10,11] We recently reported that the photochemical reaction of singlet stilbene with some tertiary amines occurs via a free-radical mechanism in nonpolar solvents and via an electron-transfer, proton-transfer mechanism in polar solvents.[12] We now report that the photochemical reaction of singlet 9-phenanthrenecarbonitrile (I) with diethylamine in nonpolar solvent yields the diethylaminyl radical exclusively, whereas reaction in polar solvent yields both diethylaminyl and 1-(ethylamino)ethyl radicals. Furthermore the conversion of aminyl to aminoalkyl radical is more rapid in polar than in nonpolar solvent. These results serve to further elucidate the mechanisms of photochemical and nonphotochemical reactions of dialkylamines.

Scheme I



Irradiation of I (0.01 M) and diethylamine (0.1 M) in nitrogen-purged benzene solution with a Pyrex-filtered medium-pressure mercury lamp results in essentially quantitative conversion to 9-(9-diethylamino-9,10-dihydro)phenanthrenecarbonitrile (II) and lesser amounts of 9-(9,10-dihydro)phenanthrenecarbonitrile (III) and *N*-ethylideneethylamine (IV) (eq 2). Chromatography (silica gel or GC) of the reaction mixture results in quantitative loss of HCN from adduct II to yield *N*,*N*-diethyl-9-phenanthrylamine (V). Irradiation of I and diethylamine in acetonitrile solution yields only III and IV. Stern–Volmer fluorescence quenching constants ($k_q\,\tau$) and quantum yields for formation of products II ($\Phi_{II} = \Phi_V$) and III are given in Table I. With use of literature values for the singlet lifetime of I (τ),[13] fluorescence quenching rate constants near the diffusion-controlled limit are calculated for both benzene and acetonitrile solution. In solvents of intermediate polarity (ethyl acetate–acetonitrile mixtures) Φ_{II} decreases continuously with increasing solvent polarity, while Φ_{III} displays a minimium value in ethyl acetate ($\epsilon = 6.0$) and increases in more polar solvents, attaining a value in acetonitrile comparable to that in benzene.



Crucial mechanistic evidence is provided by the results of irradiation of I with the deuterated amines Et_2ND and (CH_3C-

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† Dedicated to George S. Hammond on the occassion of his 60th birthday.

(1) Address correspondence to this author.

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Table I. Kinetics, Quantum Yields, and Deuterium Labeling Results

amine	solvent	$k_q\tau$,[a] M^{-1}	$10^{-9}k_q$,[b] $M^{-1}\ s^{-1}$	Φ_{II}[c]	Φ_{III}[c]	% D-10[d]	% D-9[d]
$(CH_3CH_2)_2NH$	C_6H_6	118	7.9	0.026	0.0032		
	$CH_3CO_2C_2H_5$			0.0016	0.0009		
	CH_3CN	205	8.5	0.0002	0.0030		
	$CH_3CN\text{-}D_2O$					22	69
$(CH_3CH_2)ND$	C_6H_6	107	7.1	0.015	0.0019	108	42
	CH_3CN	201	8.4		0.0030	52	25
$(CH_3CD_2)NH$	C_6H_6	106	7.1	0.027	0.0028	10	45
	CH_3CN	168	7.0	trace	0.0032	30	38

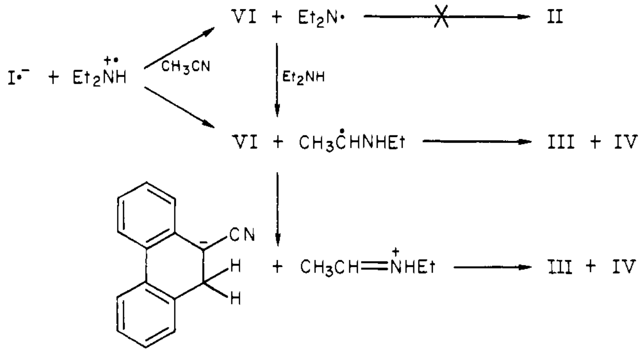
[a] Slopes of linear Stern–Volmer plots ($r^2 > 0.99$) for fluorescence quenching of I (5×10^{-5} M) by amine in nitrogen purged solutions. [b] Calculated by using reported singlet lifetimes for I in benzene (15 ns[13a]) and acetonitrile (24 ns[13b]). [c] Quantum yields for reaction of I (0.01 M) with amine (0.12 M) in nitrogen-purged solution. Monochromatic 313-nm irradiation with benzophenone–benzhydrol actinometry and product analysis by GC. [d] Deuterium content determined by ^{1}H NMR peak integration compared to undeuterated samples (±10%). Recovered I contains ca. 30% D-10 at >90% conversion.

$D_2)_2NH$ (Table I). Irradiation of I with Et_2ND in benzene solution results in quantitative and stereorandom incorporation of deuterium at C-10 in adduct II, whereas no deuterium incorporation at C-10 is obtained with $(CH_3CD)_2NH$. The extent of deuterium incorporation at C-10 and C-9 of reduction product III is reported in Table I. Irradiation of I with an equimolar mixture of Et_2NH–D_2O in acetonitrile solution produces substantially different results than irradiation with Et_2ND. Amine deuteration has little affect on either the fluorescence quenching rate constants in benzene and acetonitrile solution or the quantum yields for product formation in acetonitrile solution. The quantum yields for the formation of II and III in benzene solution are lower for Et_2ND vs. Et_2NH ($\Phi_H/\Phi_D = 1.7$) but are unaltered by $(CH_3CD_2)_2NH$.

A plausible mechanism for reaction of singlet I with Et_2ND in nonpolar solvent is shown in Scheme I. Quantitative C-10 deuteration of products II and III and the similar isotope effects on the quantum yields of formation of II and III indicate that both products are formed exclusively via initial N–H (D) atom transfer. The absence of C-10 deuteration or isotope effects for reaction of singlet I with $(CH_3CD_2)NH$ supports this conclusion. Rate-determining exciplex formation[14,15] followed by competitive exciplex decay and hydrogen transfer accounts for (a) the absence of a kinetic isotope effect on fluorescence quenching, (b) the low quantum yields for product formation, and (c) the modest isotope effect on the product formation quantum yields. Free-radical combination can account for the formation of adduct II with stereorandom C-10 deuteration, while disproportionation can account for formation of monodeuterated III. Formation of dideuterated III requires the participation of a second molecule of amine, most likely to effect the conversion of the diethylaminyl radical to the 1-(ethylamino)ethyl radical (Scheme I). Amine-catalyzed conversion of aminyl to aminoalkyl radical also provides an explanation for the absence of tetraethylhydrazine, an expected autotermination product of the diethylaminyl radical.[16] Further support for the occurrence of this process is provided by the formation of product III with ~50% deuteration at C-9, using either Et_2ND or $(CH_3CD_2)_2NH$.

A plausible mechanism for reaction in polar solvent is shown in Scheme II. Support for an electron-transfer, proton-transfer mechanism for radical-pair formation is provided by the absence of isotope effects and the increase in Φ_{III} for highly vs. moderately polar solvents.[14,15] The results of detuerium-labeling experiments indicate that α-C–H(D) and N–H(D) transfer occur to comparable extents in acetonitrile solution. The complete absence of adduct II in acetonitrile solution requires that the relative rate of radical-pair combination to yield II vs. aminyl to aminoalkyl radical conversion be much larger in benzene vs. acetonitrile solution. While little or no solvent effect would be expected for free-radical combination, spin inversion, or diffusion, abstraction of the α-C–H from amines is accelerated by charge transfer in the transition state[7] and should occur more rapidly in polar vs. nonpolar solvents. Thus both the orientation (N–H vs. α-C–H) and the fate of the initially formed radical pair are highly dependent upon solvent polarity. The utility of deuterium-labeled amines in distinguishing between N–H and α-C–H atom transfer is clearly illustrated by the present investigation.

Scheme II



The failure of singlet I and diethylamine to yield aminoalkyl radicals in nonpolar solvent is consistent with the absence of product formation from many singlet arene–trialkylamine exciplexes (including I–triethylamine) in nonpolar solvents.[2,12,14] While the preference for N–H vs. α-C–H atom transfer might be attributed to the peculiar geometry of the singlet exciplex, there are reports of aminyl radical formation in the reactions of primary and seconday amines with (a) *tert*-butoxy radicals in nonpolar solvents,[6] (b) methyl radicals in the gas phase,[4] and (c) low-temperature pulse radiolyses.[3] The frequent observation of products derived from aminoalkyl radicals may reflect the facile conversion of aminyl to aminoalkyl radicals, a process accelerated by polar solvents, high amine concentrations, and atom-transfer agents.[3-5,17] Alternatively, reactions of highly electrophilic reagents with amines may yield aminoalkyl radicals directly via an electron-transfer, proton-transfer mechanism.[7] In view of the extreme sensitivity of amine ionization potentials[18] and homolytic bond dissociation energies[11] to N and α-C alkylation, the orientation of amine atom transfer should be dependent upon amine structure as well as solvent polarity and coreactant electrophilicity.

The final aspect of our results which requires explanation is the different fates of the diethylaminyl–VI vs. 1-(ethylamino)-ethyl–VI radical pairs. The former displays a marked preference for combination, the latter for disproportionation. Radical combination of aminoalkyl radicals has ample precedent,[2,5,8,12,14] thus its absence in the present reactions is surprising. A likely explanation is found in the low ionization potential of aminoalkyl radicals[11] and the high electron affinity of radical VI.[19] One-

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(19) The electron affinity of radical VI determined from carbanion oxidation potential in acetonitrile solution is –0.1 V.

electron reduction of radical VI followed by protonation of the resulting carbanion (Scheme II) would account for the high level of C-9 deuteration of product III for reaction in acetonitrile–D_2O as well as the absence of aminoalkyl radical–VI combination product. The formation of aminoalkyl radical combination products in some amine photooxidation reactions (e.g., with stilbene[2,12] or pyridine[8]) but only redox products in others (e.g., with I or benzophenone[9]) may be determined by the electron affinity of the other member of the radical pair.[20]

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Electron-Transfer Chemistry of the Luminescent Excited State of Octachlorodirhenate(III)[†]

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Previous studies in our laboratory have established that the luminescent excited state[1] of $Re_2Cl_8^{2-}$ ($Re_2Cl_8^{2-*}$; 1.75 eV, 0.14 μs, CH_3CN soln; 25 °C)[2] is a $\delta\delta^*$ singlet.[3] Owing to our interest in photoredox processes involving polynuclear inorganic complexes,[4] we decided to explore the chemistry of $Re_2Cl_8^{2-*}$ with potential donor and acceptor molecules. These experiments have revealed that $Re_2Cl_8^{2-*}$ functions as a strong oxidant as well as a moderately good reductant in nonaqueous solutions.

Various electron acceptors (e.g., TCNE, chloranil, $PW_{12}O_{40}^{3-}$) quench the $Re_2Cl_8^{2-*}$ luminescence in nonaqueous solutions (25 °C), thereby producing $Re_2Cl_8^-$ and the reduced acceptor. A transient signal attributable to $TCNE^-$ was observed in flash kinetic spectroscopic studies[5] of dichloromethane solutions containing TCNE (10^{-3} M) and $(Bu_4N)_2Re_2Cl_8$ (10^{-4} M) (25 °C); the decay of the transient was found to follow second-order kinetics ($k = 3.2\ (7) \times 10^9\ M^{-1}\ s^{-1}$).[6] Similar flash spectroscopic experiments on the $Re_2Cl_8^{2-}$/chloranil system revealed second-order kinetic behavior for the disappearance of the photogenerated chloranil anion ($k = 1.8\ (7) \times 10^9\ M^{-1}\ s^{-1}$ in CH_3CN solution; $k = 1.5\ (2) \times 10^9\ M^{-1}\ s^{-1}$ in acetone solution).[6] Our observation that the rates of the back-reactions are near the diffusion limit suggests that very little internuclear reorganization is associated with electron transfer to the δ orbital of $Re_2Cl_8^-$.

The luminescence of $Re_2Cl_8^{2-*}$ also is quenched by secondary and tertiary aromatic amines[7] in acetonitrile solution. Neither the electronic absorption nor the emission spectrum of $Re_2Cl_8^{2-}$ changes in the presence of the quenchers, and no evidence for the formation of new chemical species was observed in flash spectroscopic or steady-state emission experiments. The measured rate constants for the steady-state quenching of the $Re_2Cl_8^{2-*}$ luminescence are given in Table I. In accord with expectation for electron-transfer quenching,[8,9] a plot of log k_q vs. $E_{1/2}(D^+/D)$ is linear for large $E_{1/2}(D^+/D)$ values (slope = 12.7 (3) V^{-1}; quenchers 3–9) and approaches a limiting value when $E_{1/2}(D^+/D)$ is small (quenchers 1 and 2) (Figure 1). We propose that the products of the quenching reaction form a strongly associated ion pair,[10] $Re_2Cl_8^{3-}\cdot D^+$; that separated $Re_2Cl_8^{3-}$ and D^+ species were not observed in flash spectroscopic experiments indicates unusually efficient back-electron-transfer.

Table I. Rate Constants for Quenching of $Re_2Cl_8^{2-*}$ by Aromatic Amines in Acetonitrile Solution at 25 °C

quencher (D)	$E_{1/2}$[a]	k_q(obsd)[b]	k_q(corr)[c]
(1) *N,N,N',N'*-tetramethyl-*p*-phenylenediamine	0.10	5.4×10^9	7.6×10^9
(2) *N,N,N',N'*-tetramethylbenzidine	0.36	2.2×10^9	2.5×10^9
(3) dimethoxydiphenylamine	0.58	1.1×10^9	1.2×10^9
(4) phenothiazine	0.59	8.4×10^8	8.8×10^8
(5) *N,N*-dimethyl-*p*-toluidine	0.70	1.3×10^7	1.3×10^7
(6) 10-methylphenothiazine	0.73	9.5×10^6	9.5×10^6
(7) diphenylamine	0.79	6.1×10^6	6.1×10^6
(8) *N,N*-diethylaniline	0.76	2.2×10^6	2.2×10^6
(9) *N,N*-dimethylaniline	0.81	1.5×10^6	1.5×10^6

[a] Reduction potentials (D^+/D, V vs. SCE) from cyclic voltammetric measurements in CH_3CN solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP). [b] Second-order rate constants ($M^{-1}\ s^{-1}$); $[(Bu_4N)_2Re_2Cl_8] = 5 \times 10^{-4}$ M; $\mu = 0.1$ M (TBAP). [c] Rate constants ($M^{-1}\ s^{-1}$) corrected for diffusion effects.

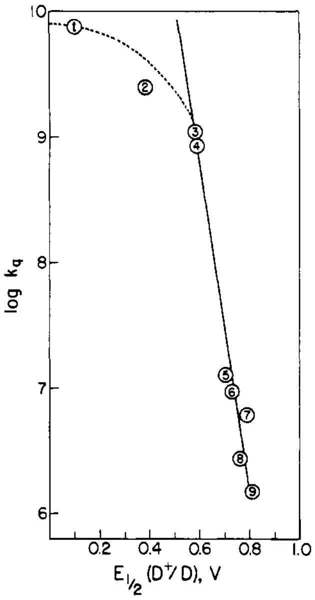

Fig 1 JA11368

Figure 1. Plot of log k_q vs. $E_{1/2}(D^+/D)$; conditions and quencher numbering as in Table I.

The two reduction potentials involving $Re_2Cl_8^{2-*}$ (–/2–*; 2–*/3–) may be estimated from the results of spectroscopic and electrochemical[11] experiments, as displayed below in the form of

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[†] Happy 60th birthday to George Sims Hammond, who first encouraged one of us (H.B.G.) to do research in inorganic and organometallic photochemistry.

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(6) Rate constants were calculated by using the following ϵ values ($M^{-1}\ cm^{-1}$): $TCNE^-$, ϵ (438 nm) 7.43×10^3 (CH_2Cl_2 solution); chloranil anion, ϵ (460 nm) 4.98×10^3 (CH_3CN solution); ϵ (466 nm) 4.92×10^3 (acetone solution).

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(9) The triplet energies of the quenchers are substantially greater than the $\delta\delta^*$ energy (1.75 eV) of $Re_2Cl_8^{2-}$, thereby ruling out an energy-transfer quenching mechanism. For example, the triplet energy of quencher 4 is 2.62 eV (Alkaitis, S. A.; Grätzel, M.; Henglein, A. *Berg. Bunsenges. Phys. Chem.* **1975**, *79*, 541–546). Selected others are as follows: quenchers 7, 3.12 eV (Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1042–1052); 8, 2.95 eV (Dubroca, C.; Loazno, P. *Chem. Phys. Lett.* **1974**, *24*, 49–54); 9, 2.99 eV (Lim, E. C.; Chakrabarti, S. K. *Chem. Phys. Lett.* **1967**, *1*, 28–31).

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