calculated from the Φ_2 values and the ratio of **2**:**3** determined from NMR spectroscopy. This was necessary because of overlap of **1** and **3** in the GLC. The **2**:**3** ratio was shown by NMR to be constant as a function of percent conversion and equal to the ratio determined by GLC at 100% conversion.

Quenching Studies. Sample preparations, photolysis, and analysis were as for the quantum yield determinations except that varying amounts of 1,3-pentadiene (0.0–4.0 *M*) were added to the solutions. Product ratios in the presence of 1,3-pentadiene were determined by NMR. Initial slopes of the Stern–Volmer plots were determined at low 1,3-pentadiene concentration (0.0–0.02 *M*).

Spectra. Relative fluorescence quantum yields were determined using a Hitachi Perkin-Elmer MPF-2A spectrofluorometer. Uv spectra were recorded on a Cary 14 or a Cary 118C spectrophotometer. The ϵ_{max} values were measured from Beer's law plots.

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(1) (a) Woods Hole Oceanographic Institution; (b) address correspondence to this author at University of Rochester; (c) Columbia University.

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(14) We thank Professor N. C. Yang for pointing this out.

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Quenching of Alkyl Ketone Fluorescence by Alkylamines

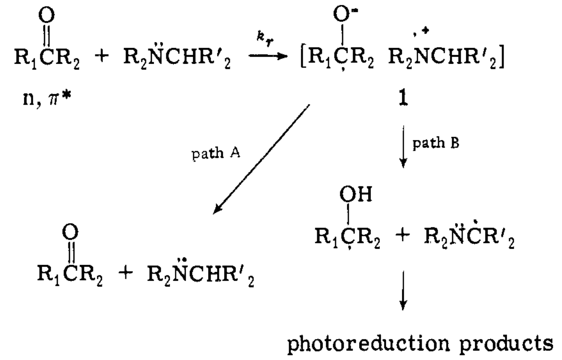
J. Christopher Dalton* and John J. Snyder

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received July 1, 1974*

Abstract: The solution phase fluorescence of 11 acyclic, cyclic, and bicyclic alkanones is quenched by diethylamine (DEA) and triethylamine (TEA). Observed bimolecular quenching rate constants (k_q) are obtained from fluorescence lifetimes ($\tau_f{}^0$) and Stern–Volmer treatments of fluorescence quenching as a function of amine concentration. The effects of ketone structure, amine oxidation potential, and the nature of the solvent on k_q values are described. The results suggest that singlet quenching occurs by interaction of the electrophilic half-vacant oxygen n orbital of the alkanone n,π^* state and the amine lone pair electrons to generate a charge-transfer complex. The rate of formation of the charge-transfer complex is very sensitive to steric effects. Acetone ^{1}n,π^* states are shown to be about an order of magnitude more reactive toward amine quenching than acetone ^{3}n,π^* states.

There has been considerable recent interest in the reactions of n,π^* excited electronic states of ketones with aliphatic and aromatic amines.[1-5] These reactions usually result in formation of ketone photoreduction products, e.g., pinacols and alcohols, and are commonly postulated to occur via the mechanism shown in Scheme I.[1] Initially a charge-transfer complex (**1**) is formed in which the electrophilic half-vacant oxygen n orbital of the ketone is the electron acceptor, and the amine nonbonding (lone pair) orbital is the electron donor. The charge-transfer complex then partitions between decay back to ground state ketone and amine (path A) and transfer of an α proton from the amine to the carbonyl oxygen (path B), forming a radical pair and leading to photoreduction products. This mechanism predicts that the reactivity of ketone n,π^* states toward amines should be a function of the amine oxidation or ionization potential (measures of the energy required to remove an electron from the amine) and the n,π^* ketone reduction po-

Scheme I



Scheme II

$$K \xrightarrow{h\nu} {}^1K \quad \text{(absorption)}$$

$${}^1K \xrightarrow{k_f} K + h\nu_f \quad \text{(fluorescence)}$$

$${}^1K \xrightarrow{k_{st}} {}^3K \quad \text{(intersystem crossing)}$$

$${}^1K + A \xrightarrow{k_{diff}} [{}^1K\cdot A] \quad \text{(formation of encounter complex)}$$

$$[{}^1K\cdot A] \xrightarrow{k_{-diff}} {}^1K + A \quad \text{(dissociation of encounter complex)}$$

$$[{}^1K\cdot A] \xrightarrow{k_r} [K\cdot A] \text{ or } [K\cdot^- A\cdot^+] \text{ or products} \quad \text{(quenching in encounter complex)}$$

tential (a measure of the energy required for addition of an electron to the ketone excited state).

The free energy change (ΔF) for charge-transfer formation between an electron donor and an excited state electron acceptor is given in eq 1

$$\Delta F = E(D/D^+) - E(A^-/A) - E_{0,0} + C \qquad (1)$$

where $E(D/D^+)$ is the oxidation potential of the electron donor in kcal/mol, $E(A^-/A)$ is the reduction potential of the ground state of the electron acceptor in kcal/mol, $\Delta E_{0,0}$ is the excited state energy of the electron acceptor in kcal/mol, and C is a constant.[6-8] The reduction potential of the excited state of the acceptor is approximated by the sum of $E(A^-/A)$ and $\Delta E_{0,0}$. This equation has been applied recently by Loutfy and Loutfy[7] and Guttenplan and Cohen[8] to charge-transfer quenching of $^3n,\pi^*$ excited states of ketones by amines and other electron donors. Loutfy and Loutfy[7] found that the observed bimolecular quenching rate constants (k_q) for quenching of ketone triplet states with electron donors increase with decreasing ΔF, reaching a limiting value of about $3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ when $E(D/D^+) - E(A^-/A) - \Delta E_{0,0}$ is less than -5 kcal/mol. A similar curve was obtained earlier by Weller and Rehm[6] who found that k_q for quenching of aromatic hydrocarbon fluorescence in acetonitrile by electron transfer leveled off at a little under $2 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ for ΔF values less than -4 kcal/mol.

The vast majority of the reactions of ketone excited states with amines studied to date have been reactions of aromatic ketones and hence, usually excited triplet states since the rapid intersystem crossing of aromatic ketone singlet states generally precludes bimolecular singlet state reactions.[9] Only a few reports of the reactivity of nonaromatic ketone n,π^* excited states toward amines have appeared.[3-5]

We report here our studies of diethylamine (DEA) and triethylamine (TEA) quenching of alkyl ketone fluorescence. We describe the effects of amine oxidation potential, ketone and amine structure, and solvent polarity on the reactivity of ketone n,π^* excited singlet states toward amines. Our results provide insight into the nature of the interaction of ketone $^1n,\pi^*$ states and alkylamines and also allow comparison of the reactivity of alkanone excited singlet and triplet states toward reaction with amines.

A generalized scheme for amine quenching of alkanone fluorescence is given in Scheme II. It is assumed that an encounter complex $[{}^1K\cdot A]$, is formed by diffusion together of the ketone $^1n,\pi^*$ state (^1K) and the amine (A). The encounter complex then undergoes irreversible quenching at a rate k_r by some process, e.g., formation of a charge-transfer complex, in competition with diffusion apart at a rate k_{-diff} to regenerate ^1K and A.[10] The Stern-Volmer expression for fluorescence quenching derived from Scheme II is given in eq 2-4,[10] where Φ_f^0 and Φ_f are the quantum yields of alkanone fluorescence in the absence and presence of A, respectively, k_{diff} is the bimolecular rate constant for diffusion, and τ_f^0 is the ketone fluorescence lifetime in the absence of amine.

$$\Phi_F^0/\Phi_F = 1 + k_q\tau_f^0[A] \qquad (2)$$

$$k_q = [k_r/(k_r + k_{-diff})]k_{diff} \qquad (3)$$

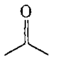
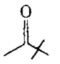
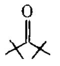
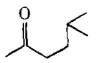
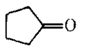
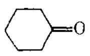
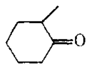
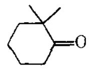
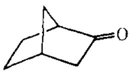
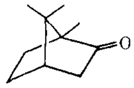
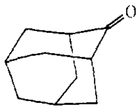
$$\tau_f^0 = 1/(k_f + k_{st}) \qquad (4)$$

We see from eq 3 that the observed rate constant for fluorescence quenching (k_q) is the product of $k_r/(k_r + k_{-diff})$, the probability that formation of an encounter complex results in quenching, and k_{diff}, the bimolecular rate constant for formation of the encounter complex. If every encounter of ^1K and A results in quenching, then k_q will equal k_{diff}, which has been recently estimated to be $2.93 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ in hexane,[12] the solvent used in most of our studies. Although the value of k_{-diff} is not well established, theoretical considerations suggest that, for normal encounter complexes, k_{-diff} is about four times greater than k_{diff}, yielding a value of about $10^{11}\ \text{sec}^{-1}$ for k_{-diff} in hexane.[11c,12]

Experimental Section

All ketones and solvents were checked for purity prior to use by uv and fluorescence spectroscopy. Acetone (Mallinckrodt Chemical Works, SpectrAR), di-*tert*-butyl ketone (Chemical Samples Co., 99%), norcamphor (Aldrich Chemical Co.), 2-adamantanone (Aldrich Chemical Co.), and hexanes (Mallinckrodt Chemical Works, SpectrAR) were used as received. *tert*-Butyl methyl ketone (Aldrich Chemical Co.) was purified by GLC using a 10 ft × 0.25 in., 15% Carbowax 20M on Chromosorb P 45-60 nonacid washed column at an oven temperature of 110°. Cyclopentanone (Eastman Organic Chemicals), bp 129°, and cyclohexanone (Mallinckrodt Chemical Works, AR Grade), bp 153.5°, were fractionally distilled. Camphor (Eastman Organic Chemicals) was sublimed. 2-Methylcyclohexanone (Eastman Organic Chemicals) was vacuum distilled, bp 53-54° (17 mm). 2,2-Dimethylcyclohexanone, a gift of Dr. Hak-Foon Chan, was purified by GLC, using a 6 ft × 0.25 in., 10% Carbowax 20M on Chromosorb P 45-60 nonacid washed column. 5-Methyl-2-hexanone (Aldrich Chemical Co.) was fractionally distilled, bp 144.5°, and then passed through a neutral alumina column. Diethylamine (Eastman Organic Chemicals) was fractionally distilled, bp 56°. For quenching studies in acetonitrile, the diethylamine was first refluxed over barium oxide and then fractionally distilled from barium oxide. This eliminated anomalous absorption in diethylamine-acetonitrile solutions. Triethylamine (Eastman Organic Chemicals), bp 89°, and 2,2,6,6-tetramethylpiperidine (Aldrich Chemical Co.), bp 156°, were fractionally distilled. Acetonitrile (Eastman, Spectra) was distilled three times from P_2O_5 (0.5-1.0%, w/v), then finally distilled from anhydrous K_2CO_3. Methanol (Mallinckrodt Chemical Works, SpectrAR) was distilled twice from CaH_2. Benzene (Mallinckrodt Chemical Works, SpectrAR) was repeatedly washed with concentrated H_2SO_4 for 3-4 hr until the acid layer no longer turned yellow. The benzene layer was next washed once with distilled water.

Table I. Quenching of Alkanone Fluorescence by Diethylamine (DEA) and Triethylamine (TEA)

Ketone[a]	τ_f^0, nsec[b]	$k_q\tau_f^0$ [c] DEA	$k_q \times 10^9$, M^{-1} sec^{-1} [d] DEA	$k_q\tau_f^0$ [c] TEA	$k_q \times 10^9$, M^{-1} sec^{-1} [d] TEA
	1.7	6.0 (0.20)	3.5	4.6 (0.12)	2.7
	2.8	3.6 (0.03)	1.3	1.9 (0.04)	0.68
	5.2	0.28 (0.03)	0.05	$\leqslant$0.02	$\leqslant$0.004
	0.35[e]	0.69 (0.03)	2.0	0.50 (0.01)	1.4
	1.6	5.9 (0.25)	3.7	4.2 (0.09)	2.6
	2.1	6.1 (0.03)	2.9	4.2 (0.06)	2.0
	2.3	3.7 (0.04)	1.6	2.1 (0.05)	0.91
	4.2	3.6 (0.09)	0.86	1.8 (0.03)	0.43
	5.3	9.9 (0.18)	1.9	6.5 (0.09)	1.2
	4.4	4.3 (0.06)	0.98	2.9 (0.07)	0.66
	8.7	12.8 (0.22)	1.5	8.0 (0.07)	0.92

[a] In hexanes with concentration (0.1–0.2 M) adjusted to give optical density equal to 0.8–0.9 at λ_{ex} (310 nm), 25.0 ± 1.0°. [b] Fluorescence lifetimes in hexanes measured by single-photon counting technique. [c] Slopes of Stern–Volmer plots for quenching of maximum fluorescence intensity (I_f^{max}) with added amine (see text). Amine concentrations: 0–0.6 M. Standard deviations (σ) are given in parentheses. [d] Observed bimolecular rate constants for amine quenching of alkanone fluorescence (eq. 2). [e] J. C. Dalton and N. J. Turro, *J. Am. Chem. Soc.*, 93, 3569 (1971). Not determined by single-photon counting.

three times with saturated Na_2CO_3, and three times with distilled water. It was then stored over anhydrous $MgSO_4$ and finally fractionally distilled over P_2O_5, the middle fraction being used.

Preparative GLC work was done either on a Varian A-90-P or a Varian Model 920 chromatograph. Optical densities at λ_{ex} (310 nm) were obtained on a Beckman DU spectrophotometer, equipped with Guilford Model 222 photometer and dual lamp source. Fluorescence spectra were measured on a Hitachi Perkin-Elmer MPF-2A spectrofluorometer. Minor corrections were made for differing optical densities at λ_{ex}. Full uv spectra were recorded using a Cary 118C spectrophotometer. Fluorescence lifetimes were measured using an Applied Photophysics Ltd. SP-1X single-photon counting lifetime apparatus with an f/4 grating monochromator, an Amperex 56 DUVP/03 photomultiplier tube, and Ortec electronics.

Results and Discussion

We have studied DEA and TEA quenching of the fluorescence of acetone (**2**), *tert*-butyl methyl ketone (**3**), di-*tert*-butyl ketone (**4**), 5-methyl-2-hexanone (**5**), cyclopentanone (**6**), cyclohexanone (**7**), 2-methylcyclohexanone (**8**), 2,2-dimethylcyclohexanone (**9**), norcamphor (**10**), camphor (**11**), and 2-adamantanone (**12**) in hexanes. The data are treated using eq 2, and the observed slopes ($k_q\tau_f^0$) of the Stern-Volmer fluorescence quenching plots for ketones **2**-**12** are given in Table I. The k_q values calculated using the slopes and measured fluorescence lifetimes (τ_f^0) are also given in Table I. We have examined solvent effects on amine quenching of alkanone fluorescence. The $k_q\tau_f^0$ and k_q values for DEA and TEA quenching of norcamphor fluorescence in hexanes, benzene, acetonitrile, and methanol are given in Table II.

The following observations can be made from the data in Tables I and II. (1) Although amines do not quench alkanone S_1 states at the diffusion-controlled rate, i.e., $k_q < k_{diff}$, amines are much better quenchers of alkanone singlets than moderately good hydrogen donors such as alcohols (k_q values for DEA and 2-propanol quenching of 2-adamantanone $^1n,\pi^*$ states are 1.5×10^9 and 1.9×10^6 M^{-1} sec^{-1},[13] respectively). (2) In hexanes, DEA is consistently a more effective alkanone fluorescence quencher than TEA. (3) Changing from a nonpolar (hexanes, benzene) to a polar nonhydroxylic (acetonitrile) solvent has little effect on the rate of amine quenching of norcamphor fluorescence. (4) Introduction of α-methyl groups on the alkanone inhibits DEA and TEA quenching of alkanone $^1n,\pi^*$ states. The ramifications of each of these observations will be discussed in detail below.

Making the reasonable assumption that k_{diff} is constant in hexanes, the substantial variations in k_q noted in Table I must reflect differences in the probability that formation of an encounter complex results in quenching. This implies that either k_r and/or k_{-diff} must be a function of ketone and amine structure. If k_{-diff} is not a function of the nature of the encounter pair, i.e., if k_{-diff} is only determined by the solvent, temperature, etc.[14] and hence is around 10^{11} sec^{-1}, then clearly the changes in k_q shown in Table I can be attributed to changes in k_r. On the other hand, if there is any interaction such as hydrogen bonding holding the encounter

Table II. Solvent Effect on DEA and TEA Quenching of Norcamphor Fluorescence

Solvent[a]	τ_f^0, nsec[b]	$k_q\tau_f^0$ [c] DEA	$k_q \times 10^9$, M^{-1} sec^{-1} [d] DEA	$k_q\tau_f^0$ [c] TEA	$k_q \times 10^9$, M^{-1} sec^{-1} [d] TEA
C_6H_{14}	5.3	9.9 (0.18)	1.9	6.5 (0.09)	1.2
C_6H_6	5.7	5.9 (0.08)	1.03	6.0 (0.08)	1.05
CH_3OH	5.1			0.6 (0.03)	0.12
CH_3CN	5.3	3.4 (0.05)	0.64	5.2 (0.04)	0.98

[a] Norcamphor concentration (0.1–0.2 M) adjusted to give optical density equal to 0.8–0.9 at λ_{ex} (310 nm), 25.0 ± 1.0°. [b] Fluorescence lifetimes measured by single-photon counting technique. [c] Slopes of Stern–Volmer plots for quenching of maximum fluorescence intensity (I_f^{max}) with added amine (see text). Amine concentration: 0.0–0.6 M. A reproducible value for DEA quenching in MeOH could not be obtained. Uvspectra of methanol solutions containing norcamphor and DEA changed as a function of time. [d] Observed bimolecular rate constants for amine quenching of norcamphor fluorescence.

complex together, i.e., forming a "sticky" encounter complex, then clearly k_{-diff} may be much less than 10^{11} sec^{-1} and may depend on the structure of the ketone and the amine, meaning that k_r cannot be directly related to k_q.

Consider the possibility that alkanone excited singlet states and amines form long-lived ($k_{-diff} \ll 10^{11}$ sec^{-1}) encounter complexes, and that the observed changes in k_q thus reflect not changes in k_r, the rate of quenching in the encounter complex, but rather changes in k_{-diff}, the rate of diffusion apart of the encounter complex. The much larger k_q value for amine quenching ($k_q \sim 10^9$ M^{-1} sec^{-1}) relative to alcohol quenching ($k_q \sim 10^6$ M^{-1} sec^{-1})[13] of alkanone fluorescence could then be due to much lower k_{-diff} values for "sticky" ^{1}n,π^*-amine encounter complexes ($k_{-diff} \sim 10^8$ sec^{-1}; $k_r \sim 10^7$ sec^{-1}) than for ^{1}n,π^*-alcohol encounter complexes ($k_{-diff} \sim 10^{11}$ sec^{-1}; $k_r \sim 10^7$ sec^{-1}). Similarly the fact that k_q for TEA quenching of di-*tert*-butyl ketone fluorescence is three orders of magnitude lower than k_q for TEA quenching of acetone fluorescence could be due to a much larger k_{-diff} value for ^{1}di-*tert*-butyl ketone-amine encounter complex ($k_{-diff} \sim 10^{11}$ sec^{-1}) than for ^{1}acetone-amine encounter complex ($k_{-diff} \sim 10^8$ sec^{-1}). Increasing steric hindrance in going from acetone to di-*tert*-butyl ketone could weaken the interaction holding the encounter complex together, thereby increasing k_{-diff} and lowering the observed k_q value. Thus we see that, if ^{1}acetone and alkylamines form long-lived ($k_{-diff} \sim 10^8$ sec^{-1}) encounter complexes, then changes in k_q with ketone and amine structure could be due to variation in k_{-diff}.

When the alkanone S_1 state-amine encounter complex is long-lived, the Stern-Volmer equation given above (eq 2-4) is no longer valid, for it assumes that $k_r + k_{-diff} \gg k_f + k_{st}$, i.e., that no normal fluorescence (or intersystem crossing) occurs from the encounter complex. If the encounter complex lives long enough for normal alkanone photophysical processes to compete with quenching and diffusion apart, then eq 5 and 6 must be added to the scheme and the modified Stern-Volmer expression given in eq 7 holds,[15] where τ_{ec} is the lifetime of the [^{1}K·A] encounter complex. This expression predicts nonlinear Stern-Volmer fluorescence quenching plots, which will have an initial slope equal to $k_{diff}\tau_{ec}k_r\tau_f^0$ and will asymptotically approach a limiting Φ_f^0/Φ_f value of $1 + k_r\tau_f^0$.[15] The limiting Φ_f^0/Φ_f value will be very large and the curvature of the Stern-Volmer plot difficult to detect, however, in cases where $k_{diff}\tau_{ec} \ll 1$. We have seen that, in order for the observed variations in k_q to be due to changes in k_{-diff}, τ_{ec} for ^{1}acetone–alkylamine encounter complexes must be on the order of 10^{-8} sec. Such a long-lived encounter complex would result in a $k_{diff}\tau_{ec}$ value of greater than 100 and would require a Stern-Volmer plot for DEA quenching of acetone fluorescence with an initial slope of 6.0 to level off at a limiting Φ_f^0/Φ_f value of <1.06. Since our fluorescence quenching plots are linear within experimental error to 0.6 M amine concentrations and Φ_f^0/Φ_f values greater than 3.0, we conclude that we are dealing with normal short-lived encounter complexes ($\tau_{ec} \ll 10^{-10}$ sec) for which $k_f + k_{st} \ll k_r + k_{-diff}$. This in turn implies that k_{-diff} is not a function of the nature of the encounter pair, and thus that the changes in k_q are due primarily to changes in k_r rather than changes in k_{-diff}. Furthermore, since k_{diff} is anywhere from one to three orders of magnitude greater than k_q, k_{-diff} must always be much larger than k_r, implying that k_q values in Table I are good estimates of relative k_r values (see eq 3).

$$[^1\text{K·A}] \xrightarrow{k_f} [\text{K·A}] + h\nu_f \tag{5}$$

$$[^1\text{K·A}] \xrightarrow{k_{st}} [^3\text{K·A}] \tag{6}$$

$$\Phi_f^0/\Phi_f = \{1 + k_{diff}(1 + k_r\tau_f^0)\tau_{ec}[Q]\} \times \frac{1}{(1 + k_{diff}\tau_{ec}[Q])} \tag{7}$$

$$\tau_{ec} = \frac{1}{(k_r + k_{-diff} + k_f + k_{st})}$$

As we have noted, the k_q values for amines given in Table I are several orders of magnitude higher than the k_q values for quenching of alkanone fluorescence by moderately potent hydrogen donors like 2-propanol.[13] Since amines would not be expected to be significantly better hydrogen donors than alcohols,[16] this suggests that quenching of alkanone ^{1}n,π^* states by amines involves primarily interaction of the electrophilic oxygen n orbital with the lone pair electrons on nitrogen rather than with the C–H bond α to the amino group. Initial interaction with the N lone pair is consistent with the generally postulated mechanisms for amine quenching of n,π^* states of ketones.[1-5] The k_q values for quenching of alkanone singlets by amines and electron rich olefins are comparable.[17,18]

One of the more interesting observations we note on examination of the k_q values in Table I is that, for every ketone in hexanes, DEA is a better fluorescence quencher than TEA. This is unusual because the lower oxidation potential of TEA [E(D/D$^+$) = 22.1 kcal/mol][7,19] might have been expected to decrease ΔF and thus increase the reactivity (k_q) of TEA relative to DEA [E(D/D$^+$) = 27.4 kcal/mol][19,20] toward charge-transfer complex formation with the electrophilic alkanone n,π^* states[1,3,5a] (see eq 1). The works of Loutfy and Loutfy[7] and Weller and Rehm,[8] however, suggest that k_q will not respond to decreases in E(D/D$^+$) if E(D/D$^+$) − E(A$^-$/A) − $\Delta E_{0,0}$ is initially <−4 kcal/mol. Using literature values for E(A$^-$/A) for acetone (−53.2 kcal/mol),[7,19] E(D/D$^+$) for DEA (27.4 kcal/mol)[7,19,20] and TEA (22.1 kcal/mol),[7,19] and $\Delta E_{0,0}$ (~85 kcal/mol), the acetone S_1 state energy, E(D/D$^+$) − E(A$^-$/A) − $E_{0,0}$ for DEA and TEA quenching of acetone fluorescence is found to be −4.4 and −9.7 kcal/mol, respectively. Charge-transfer formation between acetone ^{1}n,π^* states and DEA is thus sufficiently exothermic that it is reasonable that no further increase in k_q is observed with the decrease in E(D/D$^+$) in going from DEA and TEA. This means that we *cannot* conclude from the absence of an increase in k_q with decreasing amine ionization potential that there is minimal charge transfer in the transition state for quenching acetone excited singlets by alkylamines.[21]

Comparable conclusions are drawn from the effect of solvent on the reactivity of alkanone excited singlets toward

DEA and TEA quenching. Observed values of $k_q\tau_f^0$ and k_q for diethylamine and triethylamine quenching of norcamphor fluorescence in hexanes, benzene, methanol, and acetonitrile are given in Table II. It is clear that k_q does not change significantly in going from a nonpolar to a polar solvent. This lack of sensitivity of k_q to solvent polarity is consistent with the exothermicity [$E(D/D^+) - E(A^-/A) - E_{0,0} < -4$ kcal/mol] of charge-transfer complex formation between alkanone singlets and DEA and TEA. The quenching rate (k_q) is presumably lower in methanol because hydrogen bonding of the N lone pair electrons to the solvent hydroxyl hydrogen lowers electron density on N and reduces k_r, the rate constant for interaction of the N lone pair with the electrophilic oxygen n orbital of the alkanone n,π^* excited singlet state.[22] In benzene and acetonitrile, the k_q values for TEA quenching of norcamphor fluorescence are comparable to or greater than the k_q values for DEA quenching. It would be interesting to see if TEA is a better quencher than DEA for other alkanone singlets in acetonitrile as well. Until this is done, speculation on solvent effects on the relative k_q values for DEA and TEA would be premature.

Comparisons of the k_q values for (a) acetone (**2**), *tert*-butyl methyl ketone (**3**), and di-*tert*-butyl ketone (**4**) and (b) cyclohexanone (**7**), 2-methylcyclohexanone (**8**), and 2,2-dimethylcyclohexanone (**9**) reveal a substantial decrease in k_q with increasing α-methyl substitution on the ketone. For example, in going from **2** to **4**, k_q for DEA quenching drops two orders of magnitude from 3.5×10^9 to 5×10^7 M^{-1} sec^{-1}, while k_q for TEA quenching drops three orders of magnitude from 2.7×10^9 to $<4 \times 10^6$ M^{-1} sec^{-1}. The decreasing reactivity with α-methyl substitution on the ketone could be a steric effect and/or an inductive effect, raising the reduction potential of the ketone and reducing the n,π^* excited state electrophilicity. The failure of k_q to respond to decreasing amine oxidation potential (vide supra), however, implies that small changes in the ketone reduction potential will also not effect k_q. On the other hand, the greater sensitivity of k_q for TEA than k_q for DEA to α-methyl substitution on the ketone suggests that the k_q values are influenced by steric effects. Approach to the carbonyl group, and in particular to the electrophilic n orbital of the n,π^* excited state, is clearly sterically hindered in di-*tert*-butyl ketone, and it is reasonable that this hindrance should be more severe for TEA than for DEA. Additional evidence for the presence of steric effects is provided by a comparison of k_q values for quenching of acetone singlets by a hindered secondary amine, 2,2,6,6-tetramethylpiperidine ($k_q = 1.5 \times 10^9$ M^{-1} sec^{-1}), and DEA ($k_q = 3.5 \times 10^9$ M^{-1} sec^{-1}). A similar steric argument has been advanced by Lewis[23] to explain decreases in reactivity of alkyl aryl ketone triplets towards intermolecular hydrogen abstraction with increasing α-methyl substitution. A requirement of overlap of the amine lone pair with the half-vacant oxygen n orbital of the ketone n,π^* state for quenching in the encounter complex is consistent with our observation that, even when $E(D/D^+) - E(A^-/A) - \Delta E_{0,0}$ for charge-transfer quenching is <-4 kcal/mol, k_q is significantly less than k_{diff}. Weller[24] has noted that, in cases where "the reactants must come into contact with their mutually reactive sites" in the encounter complex in order for quenching to occur, the probability that formation of the encounter complex results in quenching is reduced.

It is also of interest to compare our data for the reactivity of acetone singlets toward alkylamines with the results for quenching of acetone triplets by alkylamines recently reported by Yip, Loutfy, Chow, and Magdzinski.[3] Our rate constant for TEA quenching of acetone fluorescence (2.7×10^9 M^{-1} sec^{-1}) is about an order of magnitude greater than the reported rate constant for TEA quenching of acetone phosphorescence. The greater reactivity of the acetone S_1 state can be attributed to the 6-8 kcal/mol higher energy of the S_1 state than the T_1 state. Since $E(D/D^+) - E(A^-/A) - \Delta E_{0,0}$ for charge-transfer quenching of the acetone T_1 state by TEA is ca. -2 kcal/mol,[7] increasing $\Delta E_{0,0}$ by 6-8 kcal/mol by going from T_1 to S_1 would be expected to lead to a substantial increase in k_q, as is observed. Turro and coworkers have reported that biacetyl S_1 states ($k_q = 2.4 \times 10^9$ M^{-1} sec^{-1} for TEA in benzene) are considerably more reactive than biacetyl T_1 states ($k_q = 5.0 \times 10^7$ M^{-1} sec^{-1} for TEA in benzene) toward quenching by amines.[5a] This difference can also be attributed to the higher S_1 energy leading to a lower ΔF value for charge-transfer formation between TEA and biacetyl S_1 states than TEA and biacetyl T_1 states. Using literature values of -33.7 kcal/mol for $E(A^-/A)$ for biacetyl[8b] and 54.9 kcal/mol for the biacetyl triplet energy,[25] $E(D/D^+) - E(A^-/A) - \Delta E_{0,0}$ for charge-transfer complex formation between biacetyl T_1 states and TEA is calculated to be ca. +1 kcal/mol.

Yip, Loutfy, Chow, and Magdzinski found the rate constant for quenching of acetone phosphorescence by both primary and tertiary amines to be independent of solvent polarity, although the k_q values were more than an order of magnitude greater for tertiary amines ($k_q \sim 3 \times 10^8$ M^{-1} sec^{-1}) than for primary amines ($k_q \sim 1.2 \times 10^7$ M^{-1} sec^{-1}).[3] Thus the reactivity of acetone S_1 states toward amines is sensitive to neither solvent polarity nor amine oxidation potential, while the reactivity of acetone T_1 states is insensitive to solvent polarity but is affected by the oxidation potential of the amine. The difference in acetone S_1 and T_1 response to amine oxidation potential is due to the lower energy of the acetone triplet state. This leads to $E(D/D^+) - E(A^-/A) - \Delta E_{0,0}$ values for DEA and TEA charge-transfer quenching of acetone triplets of ca. +4 and ca. -2 kcal/mol, respectively, and a greater k_q value for triplet quenching by TEA.[3,7] As we have seen above, the ΔF values for DEA (ca. -4 kcal/mol) and TEA (ca. -10 kcal/mol) charge-transfer quenching of acetone S_1 states are both sufficiently negative that no increase in k_q would be expected in going from DEA to TEA.

It is also enlightening to compare the reactivity of acetone and biacetyl singlet states toward quenching by alkylamines. Although the excited singlet state energy of biacetyl is more than 20 kcal/mol lower than that of acetone, as we have seen the k_q values for TEA quenching of biacetyl and acetone fluorescence are comparable. This is easily understood if the quenching occurs by a charge-transfer mechanism in both cases since the reduction potential of biacetyl (-33.7 kcal/mol)[8b] is about 20 kcal/mol lower than the reduction potential of acetone (-53 kcal/mol).[7] Thus the changes in S_1 energy and carbonyl reduction potential operate in different directions leaving ΔF and hence k_q roughly comparable for amine quenching of biacetyl and acetone singlets.[26] This argument, as well as the response of k_q to the increase in energy in going from acetone T_1 to S_1 states, strongly implicates charge-transfer interactions in the quenching of alkanone fluorescence by alkylamines.

In summary, our results demonstrate that quenching of alkanone ^{1}n,π^* states by alkylamines occurs in an initially formed encounter complex in competition with diffusion apart of the encounter complex. Steric effects suggest that the quenching mechanism requires a specific orientation of the ketone excited state and the amine in the encounter complex. Quenching appears to occur by interaction of the electrophilic half-vacant oxygen n orbital of the n,π^* excited state and the lone pair electrons on the amine to form a charge-transfer complex. Formation of charge-transfer complexes between alkanone S_1 states and alkylamines is sufficiently exothermic that amine oxidation potential and solvent polarity have little effect on the observed k_q values. Acetone n,π^* singlets are found to be about an order of magnitude more reactive than acetone n,π^* triplets toward alkylamines, an observation consistent with the lower free energy change associated with charge-transfer complex formation from the higher energy singlet state.[27]

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(26) The effect of excited state energy and $E(A^-/A)$ on k_q values for TEA quenching of carbonyl triplets has been reported. See ref 8b.

(27) NOTE ADDED IN PROOF. For a recent study of quenching of 2-pentanone singlets by aliphatic amines, see M. V. Encina, H. Soto, and E. A. Lissi, *J. Photochem.*, **3**, 467 (1974/75).