VOLUME 123, NUMBER 40
OCTOBER 10, 2001

JOURNAL
OF THE
AMERICAN
CHEMICAL
SOCIETY

## *Articles*

# Switch-Over in Photochemical Reaction Mechanism from Hydrogen Abstraction to Exciplex-Induced Quenching: Interaction of Triplet-Excited versus Singlet-Excited Acetone versus Cumyloxyl Radicals with Amines

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*Received May 16, 2001*

**Abstract:** The fluorescence and phosphorescence quenching of acetone by 13 aliphatic amines has been investigated. The bimolecular rate constants lie in the range of $10^8-10^9$ $M^{-1}$ $s^{-1}$ for singlet-excited acetone and $10^6-10^8$ $M^{-1}$ $s^{-1}$ for the triplet case. The rate data indicate that a direct hydrogen abstraction process dominates for triplet acetone, while a charge-transfer mechanism, namely, exciplex-induced quenching, becomes important for singlet-excited acetone. Pronounced stereoelectronic effects toward H abstraction, e.g., for 1,4-diazabicyclo[2.2.2]octane (DABCO), and significant steric hindrance effects, e.g., for *N*,*N*-diisopropyl-3-pentylamine, are observed. A negative activation energy ($E_a = -0.9 \pm 0.2$ kcal $mol^{-1}$ for triethylamine and DABCO) and the absence of a significant solvent effect on the fluorescence quenching of acetone are indicative of the involvement of exciplexes. Full electron transfer can be ruled out on the basis of the low reduction potential of acetone, which was found to lie below −3.0 V versus SCE. The participation of H abstraction for triplet acetone is corroborated by the respective quenching rate constants, which resemble the reaction rate constants for cumyloxyl radicals. The latter were measured for all 13 amines and showed also a dependence on the electron donor properties of the amines. It is suggested that the H abstraction proceeds directly and not through an exciplex or ion pair. Further, abstraction from N−H bonds in addition to α C−H bonds has been corroborated as a significant pathway for excited acetone. Product studies and quantum yields for photoreduction of singlet- and triplet-excited acetone by triethylamine (8% for $S_1$ versus 24% for $T_1$) are in line with the suggested mechanisms of quenching through an exciplex and photoreduction through direct H abstraction.

## Introduction

The carbonyl chromophore has played a crucial role in the development of molecular organic photochemistry, both experimentally[1−4] and theoretically.[5] While aliphatic ketones serve as prototypes for chromophores with an n,$\pi^*$ electronic configuration, state-switching to a $\pi,\pi^*$ configuration may occur for the triplet states of aromatic derivatives, which has rendered

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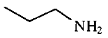
10.1021/ja011212e CCC: $20.00

ketone photochemistry a fruitful playground for mechanistic investigations. Following the pictorial description of $n,\pi^*$ excited states by Zimmerman,[1] an analogy between the reactivity of their triplet states and alkoxyl radicals in hydrogen abstraction reactions was proposed.[6,7] This has been verified for $n,\pi^*$ triplet-excited aromatic ketones, mostly benzophenone, and alkanes, alcohols, and hydrides as hydrogen donors.[3,8] The photoreactions between aromatic ketones and electron donors such as alkylbenzenes[9−12] and amines[13−17] have also revealed a competition between a "direct" hydrogen abstraction and photoinduced electron transfer, which defines another fascinating area of carbonyl photochemistry. Generally the quenching mechanism of aromatic ketones by amines proceeds via a primary electron-transfer step followed by proton transfer resulting in ketyl and aminyl or aminoalkyl radicals.[18] Consequently, a sequential electron−proton transfer gives rise to the same products as a direct H abstraction and a mechanistic differentiation requires detailed investigations.

Recent theoretical and experimental studies of the *singlet* photoreactivity of $n,\pi^*$ excited azoalkanes with electron donors, in particular amines, have revealed some new aspects.[19] These include the detailed characterization of exciplexes[20] and conical intersections,[21,22] uncommon solvent effects,[23] stereoelectronic and in particular steric effects on quenching,[24] and unprecedented selectivities toward C−H, N−H, and also O−H abstraction.[25,26] It appeared essential to scrutinize to which degree these observations could be generalized and transferred to $n,\pi^*$ singlet-excited ketones. In the present study, we have selected acetone as the simplest ketone. Surprisingly, in contrast to aromatic ketones, relatively little is known about the detailed photoreaction mechanisms of acetone with electron donors, in particular in the singlet-excited state.[27]

Acetone has a pure $n,\pi^*$ configuration and can be regarded as the basic carbonyl chromophore, if one disregards formaldehyde, which has proven a readily accessible theoretical,[5,28] but impractical experimental model. Most importantly, the fluorescence of acetone is weak but observable ($\phi_f \approx 0.1\%$),[29] such that this ketone, along with diketones such as biacetyl,[30,31] offers the challenging possibility to investigate singlet $n,\pi^*$ photoreactivity, and, moreover, to compare it to its triplet reactivity. The effect of spin multiplicity of excited acetone (singlet versus triplet) on the reactivity and efficiency of photoreactions has been previously examined for typical hydrogen donors.[32] The present study of electron donors, namely, the amines **1**−**13**, yields new insights into the above-mentioned electronic and structural aspects of singlet photoreactivity. In addition, we have observed a change in selectivity for triplet- and singlet-excited acetone, which can be rationalized in terms of a switch-over in the photochemical reaction mechanism from hydrogen abstraction to exciplex-induced quenching.



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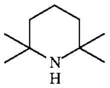

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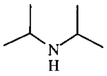

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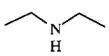

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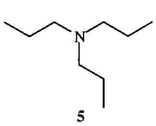

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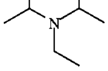

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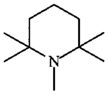

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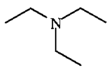

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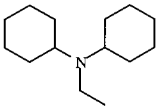

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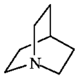

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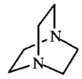

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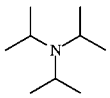

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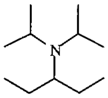

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## Experimental Section

**Materials.** Acetone was from Fluka (BioChemika for luminescence) and was used without purification. All amines except triisopropylamine (**12**) were commercially available (Fluka or Aldrich). Amine **12** was synthesized according to a literature procedure.[33] All liquid amines (except perdeuteriotriethylamine) were filtered over neutral aluminum oxide, freshly distilled, or both before use. Samples purified in this way did not show fluorescence upon excitation at 336 nm, except for **9** and **12**, which were therefore not used in the fluorescence quenching experiments. The solid amines (**10** and **11**) were purified by repeated sublimation. Solvents of spectroscopic quality were from Scharlau (acetonitrile and *n*-hexane) or Riedel-de-Haen (ethyl acetate). Water was of bidistilled quality. Di-α-cumyl peroxide (Aldrich) was purified by recrystallization from methanol.

**Fluorescence and Phosphorescence Quenching.** All quenching experiments were done with five different quencher concentrations. The quencher was added either as a stock solution or pure compound by a GC syringe. All measurements were performed at ambient temperature (298 K) unless stated differently. The bimolecular rate constants for luminescence quenching were obtained by Stern−Volmer plots, which were linear in the investigated concentration range. Amines form ground-state charge-transfer complexes *with molecular oxygen*, whose absorption extends to wavelengths above 300 nm.[34] These complexes needed to be considered in the fluorescence quenching experiments, which were performed under air to quench the phosphorescence

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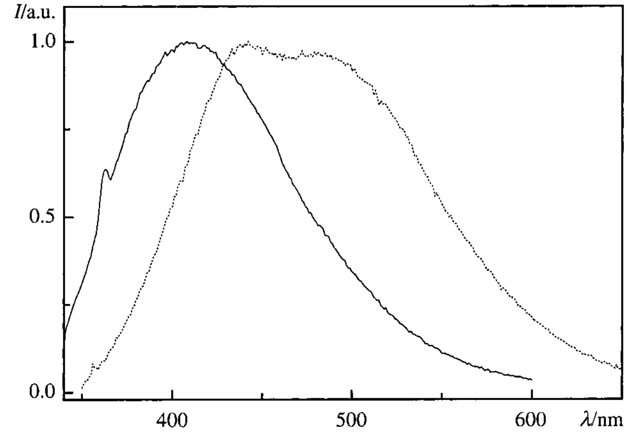

**Figure 1.** Fluorescence (solid line) and phosphorescence (dotted line) spectrum of neat acetone.

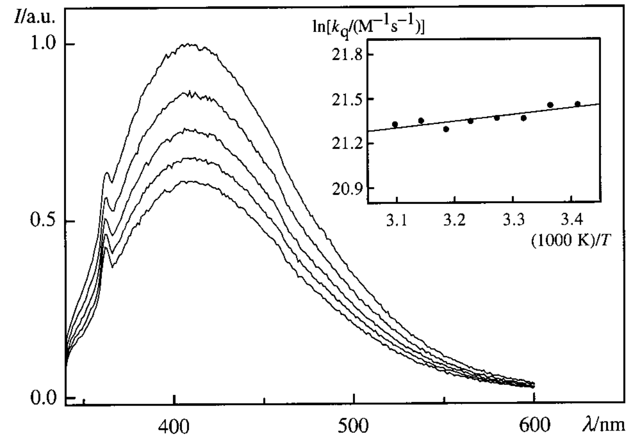

**Figure 2.** Fluorescence quenching of acetone by triethylamine (**8**). Fluorescence spectrum at different amine concentrations (0, 43, 86, 130, and 170 mM). The inset shows an Arrhenius plot (ln $k_q$ vs $1/T$) of the fluorescence quenching of acetone by triethylamine.

emission. Therefore, neat acetone was used as solvent in most cases, which allowed long-wavelength excitation (336 nm, OD = 0.16) well beyond the absorption bands of the amine−oxygen complexes. For the selected measurements in different solvents, 0.055 M acetone solutions were excited at 314 nm. The optical density at the excitation wavelength was controlled with a Hewlett-Packard 8452A diode array spectrometer. It remained constant at the excitation wavelength upon addition of the amines.

Steady-state fluorescence spectra from 350 to 600 nm (Figure 1) and fluorescence quenching effects (Figure 2) were measured with a Fluorolog Spex spectrometer from Glen Spectra Ltd. or a FLS900 fluorimeter from Edinburgh Instruments Ltd., both operated with a xenon lamp as excitation light source. They showed a maximum at 410 nm, close to the reported value of 405 nm.[35] The assignment to acetone fluorescence was confirmed by the excitation spectrum, which showed the expected maximum at 277 nm in dilute acetonitrile. A fluorescence lifetime of 1.90 ± 0.05 ns was measured in nonhydroxylic solvents such as *n*-hexane, ethyl acetate, acetonitrile, and acetone (as solvent) by single-photon counting measurements with the FLS900 fluorimeter using a nF900 nanosecond hydrogen flash lamp. This is in good agreement with previous measurements.[32] The lifetimes in $H_2O$ (1.42 ± 0.05 ns) and $D_2O$ (1.73 ± 0.05 ns) indicated a significant lifetime shortening in water and a large solvent isotope effect.

For the temperature-dependent fluorescence quenching experiments (inset of Figure 2), the sample holder was thermostated with a circulating water bath and the temperature was measured directly in the fluorescence cell (measurement under air). The fluorescence lifetimes and steady-state fluorescence spectra were measured both with quencher and without it (as reference) in a temperature range of 293−323 K. This rather small range was limited by the experimental setup at the lower end and by the low boiling point of acetone at the upper end. The concentration of the amine (e.g., 130 mM for **8**) was chosen to secure a significant quenching effect (30%) while maintaining an accurate measurement, i.e., a sufficiently strong fluorescence intensity. For the less sensitive single-photon counting measurements, an excitation wavelength of 326 nm was chosen to ensure nearly quantitative absorption of the excitation light.

The phosphorescence spectra from 350 to 650 nm (Figure 1) were recorded with a 1934D phosphorimeter from Glen Spectra Ltd. As excitation light source, a stroboscope flash lamp (FX-265 from EG&G Electro-Optics) was used. The spectra showed a maximum around 440 nm. Since this emission was quenched efficiently by oxygen and detected with a 3-$\mu$s delay, we assign it to an excited triplet state. The samples were degassed by four freeze−pump−thaw cycles before each measurement. For the quenching plots, the reported triplet lifetime of 30 ± 2 $\mu$s (for neat acetone) was used.[36] We measured virtually the same lifetime (27 ± 1 $\mu$s) by single-photon counting.

**Laser Flash Photolysis.** For the generation of cumyloxyl radicals, solutions of di-α-cumyl peroxide in acetonitrile were irradiated with a 308-nm laser pulse (Lambda Physics EMG 101 MSC excimer laser, fwhm 20 ns, pulse energy ~120 mJ). The concentration of peroxide was 0.125 M, which gave rise to OD = 0.3 at the excitation wavelength of 308 nm. The samples were degassed by three freeze−pump−thaw cycles. Homemade quartz cells (4 × 1 × 1 cm) with high-vacuum Teflon stopcocks were used for this procedure. Cumyloxyl radicals react with amines irreversibly and form products that interfere with the flash photolysis measurement. The experiments were therefore performed with a *single* laser pulse, which on this setup (4-cm optical path length, unfocused laser pulse, side-on irradiation)[37] is sufficient to obtain well-resolved kinetic decay traces. The cumyloxyl radical decays were monitored at 485 nm,[38] recorded with a transient digitizer, and analyzed by means of nonlinear least-squares fitting of monoexponential decay functions. The observed rate constants were plotted against the amine concentration to provide the bimolecular reaction rate constant as the slope ($k_{obs} = k_0 + k_q$[amine]). The value of $k_0$, the apparent unimolecular decay rate constant of cumyloxyl radicals in acetonitrile, was found to be $\sim 7 \times 10^5$ s$^{-1}$, similar to the reported value of $7.5 \times 10^5$ s$^{-1}$.[38]

**Product Studies and Quantum Yields.** All irradiations were carried out with degassed samples (three freeze−pump−thaw cycles) of varying concentrations of amine in acetone-$d_6$ in flame-sealed NMR tubes. A Hg medium-pressure arc lamp served as light source with a WG 320 cutoff filter to avoid direct excitation of the amines. The samples were analyzed by NMR spectroscopy immediately after irradiation using tetramethylsilane as internal standard (Bruker DPX 400 MHz Avance).

## Results

**Dependence on Ionization Potential and Spin Multiplicity.** The combined bimolecular quenching rate constants for singlet- and triplet-excited acetone are compiled in Table 1. Where available, they are compared with values from the literature, which are generally in very good agreement. The fluorescence quenching rate constants for acetone by amines are on the order of $10^8$−$10^9$ M$^{-1}$ s$^{-1}$, below the diffusion-controlled limit ($2.2 \times 10^{10}$ M$^{-1}$ s$^{-1}$ in acetone),[39] and show little absolute variation. The phosphorescence quenching rate constants are consistently lower and range from $10^6$ to $10^8$ M$^{-1}$ s$^{-1}$.

It is generally presumed that the quenching of excited states by amines is facilitated by charge transfer (CT) and involves either full electron transfer or quenching through exciplex

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**Table 1.** Quenching Rate Constants for Singlet- and Triplet-Excited Acetone by Amines and Reaction Rate Constants of Cumyloxyl Radicals with Amines

| | | $k_q/10^8$ M$^{-1}$ s$^{-1}$[a] | | $k_r/10^8$ M$^{-1}$ s$^{-1}$[b] |
|---|---|---|---|---|
| | amine | $^1$Me$_2$CO*[c] | $^3$Me$_2$CO*[d] | CumO$^{\bullet}$ [*t*-BuO$^{\bullet}$] |
| **1** | *n*-propylamine | 2.5 [18[e]] | 0.22 [0.13[f,g]] | 0.13 [0.17[h]] |
| **2** | 2,2,6,6-tetramethylpiperidine | 6.1 [15,[i] 7.1[j]] | 0.49 [0.38[j]] | 0.028 |
| **3** | diisopropylamine | 9.7 [16[e]] | 1.2 | 0.42 |
| **4** | diethylamine | 18 [35[i]] | 2.2 | 0.97 [0.76[k]] |
| **5** | tri-*n*-propylamine | 22 [19[e]] | 4.5 | 2.1 |
| **6** | *N*-ethyldiisopropylamine | 21 | 7.5 | 2.5 |
| **7** | 1,2,2,6,6-pentamethylpiperidine | 18 [13[j]] | 3.5 [2.3[j]] | 1.7 |
| **8** | triethylamine | 21 [12,[e] 27[i]] | 4.0 [2.9,[f] 3.9[g]] | 1.6 [1.8[h]] |
| **8-*d*$_{15}$** | perdeuteriotriethylamine | 17 | 2.6 | 1.2 |
| **9** | *N*,*N*-dicyclohexylethylamine | –[l] | 6.8 | 3.7 |
| **10** | 1-azabicyclo[2.2.2]octane | 7.9 | 0.044[m] | 0.037 [0.06[h]] |
| **11** | 1,4-diazabicyclo[2.2.2]octane | 29 | 0.83 | 0.096 [0.28[h]] |
| **12** | triisopropylamine | –[l] | 0.26 | 0.059 |
| **13** | *N*,*N*-diisopropyl-3-pentylamine | 1.6 | 0.17 | 0.034 |

[a] Bimolecular quenching rate constants in neat acetone; values in brackets are from the literature. [b] Determined by laser flash photolysis in acetonitrile; error in data is 15% (20% for values of $<0.06$); values in brackets refer to literature values for *tert*-butoxyl radicals. [c] Determined by fluorescence quenching; 10% error. [d] Determined by phosphorescence quenching; 15% error. [e] Reference 47 in benzene. [f] Reference 74 in acetonitrile. [g] Reference 49 in acetonitrile. [h] Reference 16 in benzene. [i] Reference 48 in *n*-hexane. [j] Reference 36 in neat acetone. [k] Reference 45 in benzene. [l] Samples of these amines showed impurity fluorescence at high concentrations, which did not allow a determination of the fluorescence quenching rate constants. [m] 20% error.

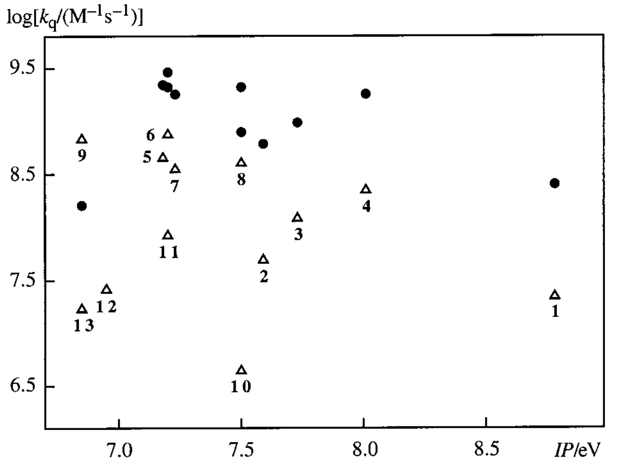

**Figure 3.** Logarithmic quenching rate constants for singlet- (filled circles) and triplet-excited (open triangles) acetone vs the adiabatic ionization potential (IP) of the amine quencher.

formation and deactivation. To probe for CT contributions to the quenching, correlations of the logarithmic quenching rate constants against the quencher ionization potential (IP) as a measure of the electron donor strength are common.[17,26,40,41] However, in the case of acetone, a plot against the adiabatic IP values of the amines[24,26] does not show a good correlation (Figure 3), although the correlation of the rate constants for fluorescence quenching (circles) shows less scatter than those for phosphorescence quenching (triangles). This is fully consistent with the reactivity–selectivity principle, which would predict a larger variation in rate constants for slower reactions, i.e., for the lower energy triplet state.

**Dependence on Amine Structure.** The most interesting effects were observed for tertiary amines. Particularly striking is the outstanding behavior of amines **12** and **13**, which are the most potent electron donors (cf. Figure 3) of all investigated amines but display quenching rate constants 1 order of magnitude lower than the other tertiary amines (Table 1). Again, this drop in reactivity is more pronounced for the triplet reaction. As clearly indicated by the absence of a reduced reactivity for amine **6**, at least three secondary alkyl groups are necessary to observe this effect. This is the first observation of a steric hindrance effect of amines toward quenching of excited ketones,[24,42] although the effect on triplet quenching may rather be due to stereoelectronic reasons (cf. Discussion). Noteworthy is also the behavior of 1,4-diazabicyclo[2.2.2]octane (DABCO, **11**). For singlet-excited acetone, **11** is the fastest quencher, presumably due to a statistical effect, since DABCO is actually a diamine. This does not hold for the triplet state, where **11** quenches even slower than triethylamine (**8**), albeit **11** has a 0.3 V lower IP than **8** (cf. Figure 3), in addition to the statistical advantage. This unexpected variation in selectivity between singlet- and triplet-excited acetone suggests immediately a change in the reaction mechanism with spin multiplicity, which will be another focal point of the Discussion.

To assess deuterium isotope effects, which should be indicative of a participation of H abstraction in the quenching mechanism, the perdeuterated derivative of triethylamine [$(C_2D_5)_3N$] was studied (entry **8-*d*$_{15}$** in Table 1). The ratio of rate constants for the protiated and deuterated amine, $k$(H)/$k$(D), revealed a small but significant isotope effect for the fluorescence quenching (1.2) and a larger value for the phosphorescence quenching (1.5). The involvement of N–H bonds in the quenching by secondary amines was established by the observation of a significant N–H/N–D deuterium isotope effect (1.7) for the quenching of singlet-excited acetone by diethylamine in $H_2O$ ($k_q = 4.7 \times 10^8$ M$^{-1}$ s$^{-1}$) and $D_2O$ ($k_q = 2.7 \times 10^8$ M$^{-1}$ s$^{-1}$) and an even larger effect (2.6) for the quenching of triplet-excited acetone by amine **2** in 10:1 mixtures per volume of acetone with $H_2O$ ($k_q = 1.0 \times 10^8$ M$^{-1}$ s$^{-1}$) and $D_2O$ ($k_q = 0.38 \times 10^8$ M$^{-1}$ s$^{-1}$).

Primary amines have stronger α C–H and N–H bonds than secondary amines[43,44] and are the least reactive in H abstraction reactions.[26,45,46] Consequently, the primary amine **1** provides another extreme since it shows the slowest quenching (1 order

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of magnitude below tertiary amines). The low IPs of primary amines may also contribute to the presently observed very low reactivity, which is in contrast to a previous study, in which a faster fluorescence quenching of acetone by primary amines (similar to tertiary amines) has been reported.[47] It should be noted that N−H abstraction from primary amines has been established in the quenching of aromatic ketones by amines.[46]

**Temperature Dependence of Fluorescence Quenching.** For triethylamine (**8**) and DABCO (**11**) the temperature-dependent quenching rate constants for singlet-excited acetone were measured between 293 and 323 K. To calculate rate constants at each temperature, the lifetime of neat acetone was measured as a control and reference but it remained quite constant within the examined temperature range ($1.90 \pm 0.05$ ns). Both amines displayed an interesting behavior: the quenching became slower when the temperature increased; i.e., this photoreaction displays a negative activation energy (see inset of Figure 2). The $E_a$ values resulting from Arrhenius plots ($r \geq 0.85$, $n = 8$) are the same for both **8** and **11**, $-0.9 \pm 0.2$ kcal mol$^{-1}$. The difference in the absolute rate constants (Table 1) is therefore manifested in the $A$ factors: $\ln[A/(\mathrm{M}^{-1}\ \mathrm{s}^{-1})] = 19.9 \pm 0.4$ for **8** and $20.3 \pm 0.3$ for **11**.

**Solvent Dependence.** For **8**, the fluorescence quenching was investigated in solvents of increasing polarity: *n*-hexane, ethyl acetate, acetone, acetonitrile, and water. The rate constants of $2.5 \times 10^9$, $2.1 \times 10^9$, $2.1 \times 10^9$, $2.4 \times 10^9$, and $1.3 \times 10^9$ M$^{-1}$ s$^{-1}$, respectively, revealed that the reactivity of singlet-excited acetone toward triethylamine is not influenced by the solvent within error (±10%), except for the drop in water, which is presumably due to a stabilization of the amine by hydrogen bonding, as previously suggested for other systems.[48] A similar solvent effect has been previously reported for the quenching of triplet acetone by triethylamine.[49] The lack of a significant solvent effect on the fluorescence quenching in nonhydroxylic solvents was also confirmed for amines **6** and **13**.

**Energetics of Electron Transfer.** The driving force for photoinduced electron transfer ($\Delta G_{\mathrm{et}}$) can be estimated according to Rehm and Weller as $\Delta G_{\mathrm{et}} = E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - E^* + C$.[50] $E^*$ is the excitation energy of the acceptor, i.e., 3.69 and 3.38 eV for singlet- and triplet-excited acetone, respectively,[32] and $C$ denotes a solvent-dependent Coulomb term, which is frequently neglected in polar solvents such as acetonitrile or acetone. The $E_{\mathrm{ox}}(\mathrm{D})$ values are oxidation potentials of the donors, i.e., the amines, and $E_{\mathrm{red}}(\mathrm{A})$ is the reduction potential of the acceptor, i.e., acetone. The former are available for most amines from previous studies[24,51,52] but follow the same trend as the IPs, which are often preferred for qualitative discussion and correlation (Figure 3).[53] The reduction potential of acetone has also been reported, but the values show a rather large scatter. Loutfy et al. reported a value of $E_{\mathrm{red}} = -2.31$ V versus SCE,[54,55] Albisson et al. stated a potential of $E_{\mathrm{red}} = -2.84$ V versus SCE,[56] and Dalton et al. could not access this potential on their setup and suggested an even lower value ($E_{\mathrm{red}} \leq -3.0$ V versus SCE).[57] We have also evaluated the reduction potential of acetone experimentally by employing a hanging mercury drop electrode setup in dry deaerated acetonitrile and *N*,*N*-dimethylformamide with tetra-*n*-butylammonium perchlorate (0.1 M) as supporting electrolyte.[58] This method has proven suitable to determine the very negative reduction potentials of bicyclic azoalkanes, which are as low as −2.9 V versus SCE.[23,24,59] Our finding clearly matches the observation described by Dalton et al. No reduction of acetone was detected in the accessible potential range, thus confirming $E_{\mathrm{red}} \leq -3.0$ V versus SCE.

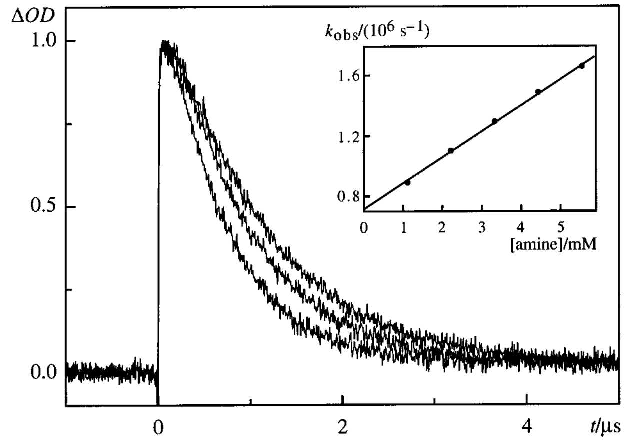

**Figure 4.** Kinetic traces ($\lambda_{\mathrm{obs}} = 485$ nm) for the decay of cumyloxyl radicals in degassed acetonitrile at different concentrations of 1,2,2,6,6-pentamethylpiperidine ([**7**] = 1.1, 2.2, and 4.4 mM). The inset shows the corresponding kinetic quenching plot.

Even for the most easily oxidizable quenchers used in this work (tertiary amines, $E_{\mathrm{ox}} \sim 0.7$ V)[24] and singlet-excited acetone as the highest energy acceptor thermoneutral $\Delta G_{\mathrm{et}}$ values result. The oxidation potentials of secondary amines, e.g., 1.0 V for **2**[52] and 1.3 V for **4**,[51] are even less favorable. Due to the lower excitation energy of triplet acetone, $\Delta G_{\mathrm{et}}$ is ~0.3 eV for the strongest donors, such that a full electron transfer appears unlikely in both cases. Unfortunately, several previous studies have used the highest reported value ($E_{\mathrm{red}} = -2.31$ V) for the reduction potential of acetone, which leads to an overestimation of the driving force for electron transfer by ~0.7 eV.[48,49,54,60−63] The conclusions based on this value should be reconsidered accordingly.

**Reactivity of Amines toward Alkoxyl Radicals.** To compare the reactivity of excited acetone with that of alkoxyl radicals, di-α-cumyl peroxide was photolyzed in acetonitrile at 308 nm and the resulting cumyloxyl radicals were monitored at 485 nm (Figure 4). Usually alkoxyl radicals, e.g., *tert*-butoxyl radicals,

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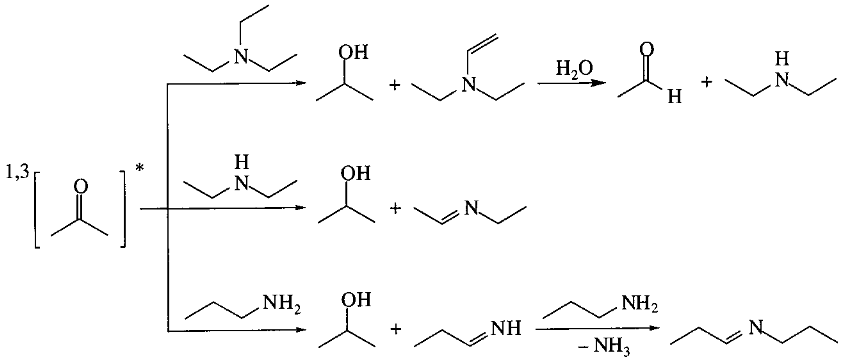
**Scheme 1**



do not absorb in the visible wavelength range, such that competitive quenchers such as diphenylmethanol have been previously employed as probes to indirectly determine their reactivity by flash photolysis.[16] The recent observation by Lusztyk and co-workers that aryl-substituted alkoxyl radicals show absorption bands in the visible region now allows direct measurements of alkoxyl radical reactivity by conventional flash photolysis.[38] Acetone, which has been used as solvent for the quenching studies, cannot be employed for di-α-cumyl peroxide photolysis, since it is opaque in this region. Hence, acetonitrile was chosen as a solvent with a polarity comparable to acetone. Table 1 includes the measured rate constants, which vary over a large range from $10^6$ to $10^8$ $M^{-1}$ $s^{-1}$ and compares it to data available for *tert*-butoxyl radicals. There is a good absolute and relative agreement between the data, indicating that α-phenyl substitution hardly affects the reactivity of tertiary alkoxyl radicals toward amines.

**Product Studies.** Several product studies on the photoreduction of n,π*-excited aromatic ketones (in their triplet state)[14,64,65] and azoalkanes (singlet and triplet excited)[59,66] are available in the literature. Triethylamine, diethylamine, and *n*-propylamine were selected as representative reactants, since some derived photooxidation products have been identified in the previous studies. These experiments were also aimed to compare the efficiency of the singlet and triplet photoreaction in terms of photoproduct quantum yields.

A sufficient quenching of the short-lived singlet-excited acetone required a large amount of amine (1 M), which complicated NMR analysis, such that this type of experiment was only performed for triethylamine. The quantum yields and identified products are shown in Scheme 1 and summarized in Table 2. Product studies of the triplet reaction were straightforward, since less than 100 mM amine in deuterated acetone ensured quantitative quenching of the triplet state (>98%), but left the singlet-excited state unaffected (<5%). For both spin states of acetone, the same products are expected, as recently shown for singlet- and triplet-excited azoalkanes.[59,66] This expectation was corroborated for triethylamine as quencher.

**Table 2.** Identified Photoproducts[a] and Photoreduction Quantum Yields in the Photolysis of Acetone by Amines[b]

| | | $\phi_r$ [c] | |
|---|---|---|---|
| amine | products | $^1Me_2CO^*$ | $^3Me_2CO^*$ |
| $(C_2H_5)_3N$ | $(CD_3)_2CHOH$<br>$(C_2H_5)_2NH$<br>$CH_3CHO$ | 0.08 | 0.24 |
| $(C_2H_5)_2NH$ | $(CD_3)_2CHOH$<br>$C_2H_5N{=}CHCH_3$<br>$C_2H_5N(H)CH(CH_3)-C(CH_3)_2OH$ | | 0.51 |
| $n$-$C_3H_7NH_2$ | $(CD_3)_2CHOH$<br>$C_3H_7N{=}CHC_2H_5$ | | 0.04 |

[a] Identified by the following $^1$H NMR shifts (in ppm, acetone-$d_6$): $(C_2H_5)_2NH$ ($CH_3$ 1.01, t, $J = 7.1$ Hz; $CH_2$ 2.57, q, $J = 7.1$ Hz); $CH_3CHO$ ($CH_3$ 2.13, d, $J = 2.5$ Hz; CHO 9.72, m); $C_2H_5N{=}CHCH_3$ [$CH_3$(CH) 1.83, dt, $J = 5.1$, 1.0 Hz; $CH_2$ 3.30, qt, $J = 7.1$, 1.0 Hz; CH 7.67, qt, $J = 5.1$, 1.5 Hz]; $(C_2H_5)_2N(H)CH(CH_3)-C(CH_3)_2OH$ (CH 3.19, q, $J = 7.1$ Hz); $(CD_3)_2CHOH$ (CH 3.87, s); $C_3H_7N{=}CHC_2H_5$ [CH 7.68, t, $J = 4.6$ Hz]. [b] The photolysis was carried out by exciting acetone-$d_6$ as solvent. [c] Quantum yield for the formation of 2-propanol, determined by using acetone-$d_6$/tributyltin hydride as actinometer ($\phi_r = 1$ [72]); error in data is 20%.

In the photoreaction with triethylamine (Table 2, Scheme 1), the primary formed enamine was not detected, but rather its hydrolysis products, i.e., diethylamine and acetaldehyde, resulting from a follow-up reaction with residual water in the commercial deuterated acetone solvent.[59,66] These products were identified by comparison with authentic samples. Roth and Manion previously evidenced the formation of the intermediary enamine during photolysis of acetone-$d_6$ in the presence of triethylamine by CIDNP.[67] Diethylamine and *n*-propylamine as reducing reagents were oxidized to the corresponding imines (Table 2, Scheme 1), which were identified by comparison with literature NMR data.[68,69] Cross-coupling products are quite common for photoreductions in ketone/amine systems.[67,70] Indeed, for the secondary amine, signals of the cross-coupling product of aminoalkyl and ketyl radicals were detected, i.e., *N*-(2-hydroxy-1,2-dimethylpropyl)-*N*-ethylamine. No spectrum for this compound was available but that of the derivative *N*-(2-hydroxy-1,2-dimethylpropyl)glycine.[71] The initial photoreduction product of acetone is 2-propanol in all cases.

**Quantum Yields.** Since 2-propanol is a common photoproduct of all studied photoreactions (Table 2), the characteristic NMR absorption at 3.87 ppm (α C–H) was used to compare the relative quantum yields for formation of this product (see Table 2). This can be taken as a measure of the overall photoreaction efficiency in a first approximation. By comparing the formation of 2-propanol for triplet quenching (10 mM triethylamine) and singlet quenching (1 M triethylamine), a 3 times higher efficiency for the triplet reaction was noticed. This

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result was obtained after correction of the data of the singlet reaction for participation of triplet acetone. This was an important pathway (20%) even at the high amine concentration (1 M) employed. The absolute quantum yields for the formation of 2-propanol (24 ± 5% for the triplet and 8 ± 2% for the singlet) were calculated by using the photoreduction of triplet acetone by tributyltin hydride as an actinometer system, which is known to proceed with unit efficiency.[72] This results in the interesting scenario that the photoreduction is more efficient at *lower* amine concentrations. A similar finding has been made for the photoreduction of $\pi,\pi^*$-excited fluorenone by amines.[73]

The lower-than-unity quantum yields for the triplet reaction are presumably due to regeneration of the reactants from intermediary radical pairs by hydrogen back transfer as previously suggested in the photoreaction of triplet acetone with amines[74] and hydrogen donors.[75] The quantum yield for the singlet reaction is even lower than for the triplet case (Table 2). This is in agreement with the findings for the photoreaction of acetone with hydrogen donors.[32] As suggested by recent studies, the occurrence of conical intersections along the pathway for H abstraction[21,22] or in the close vicinity of exciplexes[20] is responsible for the low efficiency of the singlet photoreaction. For singlet-excited acetone, quenching is indeed presumed to involve exciplex formation and subsequent deactivation (cf. Discussion), which could account for the reduced quantum yields.

## Discussion

The earliest observations of acetone luminescence were made by Gelbke,[76] Damon and Daniels,[77] and Crone and Norrish.[78] Following the first time-resolved solution studies by Porter et al.,[79] the earliest systematic studies on the bimolecular quenching of its luminescence were described by Yip and co-workers,[49,75] Turro et al.,[2] and Scaiano and co-workers.[74] The mechanism of the fluorescence and phosphorescence quenching of acetone by amines is the focus of the present study. A mechanistic study comparing the reactivity of singlet- and triplet-excited acetone with an extended set of amines is not available. Since acetone undergoes efficient intersystem crossing, most previous studies have concentrated on its long-lived phosphorescent triplet state.[36,49,74] Only three studies have dealt with the fluorescence quenching of acetone by amines.[36,47,48]

The structure of the Discussion is such that we will first question to which degree the quenching rate constants of triplet- and singlet-excited acetone are consistent with the idea of an alkoxyl radical-type reactivity. The latter was evaluated through the reaction rate constants of cumyloxyl radicals, which will be discussed beforehand.

**Reactivity of Cumyloxyl Radicals.** The comprehensive data set for the reactivity of cumyloxyl radicals with amines (Table 1) allows us to draw some general conclusions. First, the low reactivity of some amines stands out, which can be accounted for in terms of well-established structural or stereoelectronic effects. Expectedly, the amine **2**, which lacks reactive, i.e., readily abstractable,[45] α C−H hydrogens reacts very slowly (Table 1), presumably by N−H abstraction (see below). The drop in reactivity for the amines **10**−**13** can be attributed to stereoelectronic effects, which become operative in direct H abstraction reactions.[16,80] The abstractable hydrogens of DABCO (**11**), for example, are frozen in a conformation (60° angle relative to the nitrogen lone pair) that prevents an efficient stabilization of the resulting radical by a 3-electron−2-center interaction.[42,81] The same conclusion is valid for 1-azabicyclo-[2.2.2]octane (**10**). A stereoelectronic situation applies also for the two amines **12** and **13**, which are nearly planar due to steric repulsion of the alkyl groups. In these amines, the α-hydrogens adapt an orthogonal orientation relative to the nitrogen lone pair.[33,82] The lower reactivity of amines **12** and **13** compared to DABCO may reflect the angular dependence of the stereoelectronic effect (90° vs 60°).[80]

Apart from the structurally or stereoelectronically distinct amines **2** and **10**−**13**, the reactivity of cumyloxyl radicals reveals a correlation with the IP values of the amines ($\log k_r = 13.6 - 0.73\mathrm{IP}$, $r = 0.939$, $n = 8$). This supports the notion previously expressed for *tert*-butoxyl radicals in high-temperature gas-phase experiments, namely, that H abstraction from amines depends on the donor ability,[83] i.e., involves some degree of charge transfer. Note also that the reactivity difference between **10** and **11**, both toward cumyloxyl (Table 1) and *tert*-butoxyl radicals,[16] is larger than expected on purely statistical grounds (factor 2), which provides another indication for CT contributions to this radical reaction, since the IP of **10** lies above that of **11** (Figure 3). Favorable CT interactions may also be responsible for the interesting fact that *tert*-butoxyl radicals react as fast with triethylamine (**8**) as with tributyltin hydride (1.8 versus $2.2 \times 10^8$ M$^{-1}$ s$^{-1}$)[16,84] although the bond dissociation energy of the latter is ∼17 kcal mol$^{-1}$ lower (91 kcal mol$^{-1}$ for α-C−H of **8**[85] and 74 kcal mol$^{-1}$ for Sn−H[86]). It follows that even the alkoxyl radical reaction shows a dependence on the electron donor strength of the amine, presumably due to the involvement of CT contributions in the transition state, i.e., the "polar effect" in radical reactions.[87,88] This leads us to the important conclusion that a correlation of the quenching rate constants of $n,\pi^*$-excited states and the ionization potentials of amines is expected even when excited-state specific CT stabilizations, i.e., exciplexes or photoinduced electron transfer, do not apply.

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(85) The following bond dissociation energies ($D$, 298 K) and enthalpies of formation in the gas phase ($\Delta H_f$, 298 K) were used for the calculation of the reaction enthalpies: $D$ (α C−H in triethylamine) = 90.7 kcal mol$^{-1}$ (from: Dombrowski, G. W.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Org. Chem.* **1999**, *64*, 427−431.), and $D$ (α C−H in *i*-PrOH) = 89.0 kcal mol$^{-1}$ (from: Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311−3314.), $\Delta H_f$ (H$^\bullet$) = +52.1 kcal mol$^{-1}$ (from: Weast, R. C., Lide, D. R., Astle, M. J., Beyer, W. J., Eds. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1990.), $\Delta H_f$ (acetone) = −52.2 kcal mol$^{-1}$ (from: Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc*. **1991**, *113*, 3447−3450.), and $\Delta H_f$ (*i*-PrOH) = 65.2 kcal mol$^{-1}$ (from: Buckley, E.; Herington, E. F. G. *Trans. Faraday Soc.* **1965**, *61*, 1618−1625.).

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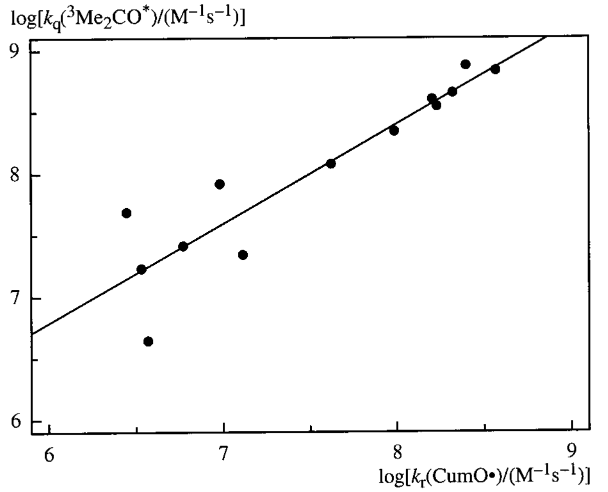

**Figure 5.** Correlation of the logarithmic quenching rate constants for triplet acetone vs the logarithmic reaction rate constants for cumyloxyl radicals.

**Quenching of Triplet Acetone.** The observed phosphorescence quenching rate constants are close to those for the interaction of alkoxyl radicals with aliphatic amines, a reaction for which a direct H abstraction operates.[83,89] In fact, the reactivity of acetone in the excited triplet state can be nicely correlated for all amines with the reaction rate constants of cumyloxyl radicals (Figure 5, $\log k_q = 1.95 + 0.807 \log k_r$, $r = 0.920$, $n = 13$). The comparable absolute reactivity of the radical and the excited state leads us to the interesting[3,6−8] but for amines uncommon conclusion that the same mechanism, i.e., direct H abstraction by the oxygens, is operative. The structural and stereoelectronic effects discussed for cumyloxyl radicals apply accordingly also to triplet acetone. The slightly but consistently higher reactivity of triplet acetone compared to the alkoxyl radicals (Table 1) has been previously ascribed to a slightly more favorable reaction thermodynamics.[8] In addition, steric factors may contribute since the approach of tertiary alkoxyl radicals may be somewhat more hindered in the transition state than that of acetone due to the additional alkyl or aryl substituent.

To substantiate a direct H abstraction, the deuterium isotope effect was measured for perdeuterated triethylamine and values of 1.5 for triplet acetone and 1.4 for cumyloxyl radicals were obtained. While these values are not very large, presumably due to the fast reaction rates, the agreement between these two values and the value found by Griller et al. for *tert*-butoxyl radicals (1.4) is very satisfying in view of the proposed common mechanism.[16] Finally, the absence of a solvent effect for triplet acetone[49] is also in line with a direct H abstraction and is expected from the presumed radical-type transition state. The conclusion that the quenching of triplet acetone by amines proceeds via a rather pure radical-type direct H abstraction—without excited-state-specific CT interactions—is quite important since exciplexes or photoinduced electron transfer have nearly always been invoked in the quenching of excited states by amines. Support for the absence of significant CT interactions stems also from the result that the reactivity of triplet acetone toward **8**, and tributyltin hydride is similar (4.0 versus $5.4 \times 10^8$ M$^{-1}$ s$^{-1}$),[31] as was the case for *tert*-butoxyl radicals (see above).

**α C−H versus N−H Abstraction.** Since the quenching of triplet acetone by amines reflects a direct H abstraction reactivity, the rate constants can be employed to assess the inherent relative reactivity of this excited state toward α C−H and N−H hydrogens and to compare it with that of alkoxyl radicals. 2,2,6,6-Tetramethylpiperidine (**2**) lacks abstractable α C−H hydrogens such that its interaction proceeds mainly through N−H abstraction, as confirmed by the large N−H/N−D deuterium isotope effect for this amine (2.6). Amine **2** and **8** were therefore chosen as prototypal amines that undergo N−H and α C−H abstraction, and their rate constants were compared. For cumyloxyl radicals, the ratio of rate constants for amine **8** normalized to the number of α C−H bonds, i.e., divided by 6, and amine **2** amounts to 9.5, indicating a preferable reactivity with the α C−H bonds as previously reported for the reaction of *tert*-butoxyl radicals with amines.[45] For triplet acetone, the same ratio is merely 1.4, indicating a very similar reactivity toward these two types of hydrogens. In fact, the phosphorescence quenching rate constants for the other two secondary amines **3** and **4** can be quite reliably predicted if one assumes the same rate constant increment of $(0.4-0.5) \times 10^8$ M$^{-1}$ s$^{-1}$ per reactive α C−H or N−H bond. The contrasting reactivity of **2** renders this amine also one of the few outliers in the correlation in Figure 5.

The comparable reactivity of triplet acetone toward α C−H and secondary N−H bonds is important since it is generally presumed that n,$\pi$*-excited states behave as *electrophilic* species.[1,3,7,90] However, we have recently documented that n,$\pi$* singlet-excited azoalkanes undergo even a preferential, albeit thermodynamically disfavored attack, at the “electrophilic” amino hydrogens rather than at the “nucleophilic” alkyl hydrogens.[19,26] A similar change in reactivity may apply for excited acetone and result in a relatively high tendency for N−H abstraction. The high reactivity toward N−H bonds is also indicated by the relatively high rate constants for the secondary amines observed in the present and an earlier[74] study.

**Quenching of Singlet-Excited Acetone.** Abstraction from C−H and N−H bonds is also involved for singlet-excited acetone as evidenced by the significant deuterium isotope effects for the secondary and tertiary amines **4** and **8** (cf. Results) as well as the observed photoproducts (Table 2). However, singlet-excited acetone displays a distinctly different reactivity pattern than triplet acetone. The most striking distinction between fluorescence and phosphorescence quenching is the fact that 1,4-diazabicyclo[2.2.2]octane (**11**), a good electron donor, shows only medium reactivity toward triplet acetone but is the fastest fluorescence quencher. Such a change in selectivity toward quenchers signals a change in reaction mechanism. In fact, the correlation against the reaction rate constants for cumyloxyl radicals deteriorates (Figure 6, $\log k_q = 6.32 + 0.36 \log k_r$, $r = 0.678$, $n = 11$) compared to triplet acetone. Moreover, the high absolute quenching rate constants for tertiary amines stand out. For example, the reactivity of singlet-excited acetone toward **8** now exceeds that for tributyltin hydride (2.1 vs $1.0 \times 10^9$ M$^{-1}$ s$^{-1}$),[31] just opposite to the result for the “pure” hydrogen-abstracting agents (alkoxyl radicals and triplet-excited acetone; see above). The combined findings point to the participation of CT-induced quenching in addition to H abstraction. The pronounced jump in reactivity for certain amines such as **11** further suggests that CT may even become the major quenching pathway of singlet-excited acetone, in particular for tertiary amines. It should be noted that the correlation of the fluorescence quenching rate constants against the IP for amines **1**−**13** is also qualitatively improved compared to triplet acetone (Figure 3),

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[89] Encina, M. V.; Lissi, E. A. *Int. J. Chem. Kinet.* **1978**, *10*, 653−656.

[90] Naguib, Y. M. A.; Steel, C.; Cohen, S. G.; Young, M. A. *J. Phys. Chem.* **1987**, *91*, 3033−3036.

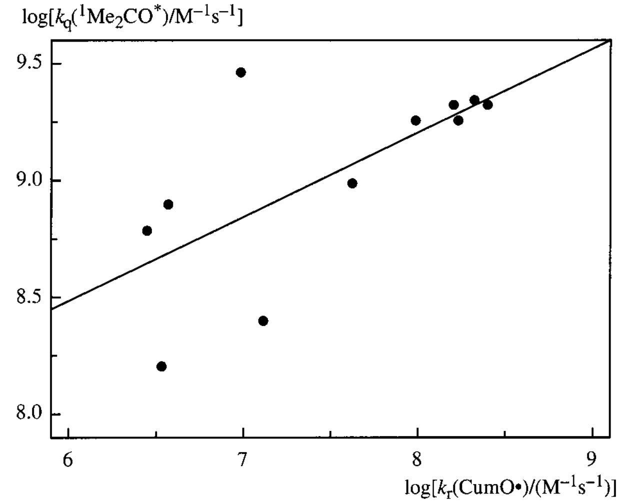


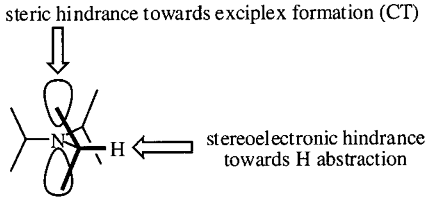
**Figure 6.** Correlation of the logarithmic quenching rate constants for singlet-excited acetone vs the logarithmic reaction rate constants for cumyloxyl radicals.

but a large scatter remains, which reveals again the importance of structural effects of the amines in addition to their electron-donating properties.

Since a full electron transfer resulting in radical ions can be ruled out on the basis of the very low reduction potential of acetone (which has been previously underestimated; cf. Results), a CT complex, i.e., an exciplex, was presumed. The measured negative activation energies in the fluorescence quenching of acetone by amines also speak against a simple unistep quenching mechanism and suggests an intermediary complex like an exciplex.[91−94] As recently demonstrated,[20,24] the geometries of exciplexes between n,$\pi^*$-excited states are characterized by the formation of a three-electron-two-center bond between the half-vacant n orbital of the excited state and the lone pair of the amine, i.e., $R_2C{=}O{\cdots}NR_3$. Related exciplex structures have been calculated by semiempirical (UHF-PM3)[23,24] as well as high-level ab initio methods.[20] The UHF-PM3 method predicts the formation of a slightly endothermic (2.6 kcal mol$^{-1}$) triplet exciplex between acetone and triethylamine with an O$\cdots$N bond distance of 1.91 Å, a C=O$\cdots$N bond angle of 126°, and a C−C=O$\cdots$N torsion angle of 180°.

The very low rate constants for amines **12** and **13** can be in part accounted for in terms of the stereoelectronic hindrance toward H abstraction discussed above. However, comparison of the reactivity of the amines **12** and **13** with that of **11**, which also displays a stereoelectronic effect, reveals that this explanation cannot account for the entire drop in reactivity of these amines toward singlet-excited acetone. For cumyloxyl radicals and triplet acetone, the rate constants for **11**−**13** are quite similar (factor 2−4 difference), while for singlet-excited acetone the difference between **11** and **13** is more than 1 order of magnitude, despite the much faster absolute quenching by these amines. Additional effects must be invoked to account for this change in relative reactivity. In fact, we have recently demonstrated that the amines **12** and **13** exhibit not only a *stereoelectronic hindrance* toward H abstraction but also a *steric hindrance* toward exciplex formation[24] as a consequence of the steric repulsions of the three alkyl groups (Scheme 2).

**Scheme 2**



Since exciplex formation is considered to become important or even dominant for singlet-excited acetone, steric effects may slow down the quenching by amines **12** and **13** but not by amines **10** and **11**, which are unique in that they display stereoelectronic but no steric hindrance. This renders the reactivity of the amines **10** and **11** crucial to assess the relative contributions of the different quenching mechanisms, namely, exciplex formation and H abstraction. On the other hand, the amines **12** and **13** are important probes to differentiate between exciplex formation (CT) and full electron transfer.[95] Large steric hindrance effects are only expected for exciplex-induced quenching[24] but not for photoinduced electron transfer. For example, the sterically hindered, but electron-rich amines **12** and **13** quench triplet benzophenone by electron transfer and react even faster than unhindered amines, since the electron-transfer process does not respond to steric hindrance.[81]

The observed lack of a solvent effect on the fluorescence quenching does not speak against an exciplex intermediate but against a full electron transfer. At first glance, the invariance of the rate constants in solvents of different polarity seems not to support the participation of CT-induced quenching, for which one generally expects an acceleration with increasing solvent polarity. However, we have recently demonstrated that even an "inverted" solvent effect can be consistent with CT-induced quenching if the increase in dipole moment in the exciplex compared to the reactants is relatively small as a consequence of a low degree of CT.[20,23] This explanation holds for the singlet exciplexes of acetone and amines, and, in fact, the previous semiquantitative treatment[96] suggests a solvent effect between that expected for benzophenone ("regular" effect) and azoalkanes ("inverted" effect). This is well in line with the lack of a solvent effect for acetone and signifies that the amount of CT in the case of singlet-excited acetone falls between that expected for triplet benzophenone and singlet-excited azoalkanes.

Akin to the situation for n,$\pi^*$-excited azoalkanes, we presume that the follow-up reaction of the exciplex involves deactivation at a close-lying conical intersection.[20,24] Electron transfer from the exciplex, i.e., "inner-sphere" electron transfer,[97] appears unlikely in view of the unfavorable thermodynamics. As a second reaction of the exciplex, an "exciplex-mediated" H

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[91] Yang, N. C.; Hui, M. H.; Shold, D. M.; Turro, N. J.; Hautala, R. R.; Dawes, K.; Dalton, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3023−3033.

[92] Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Faraday Trans 1* **1983**, *79*, 221−234.

[93] Kuzmin, M. G. *Pure Appl. Chem.* **1993**, *65*, 1653−1658.

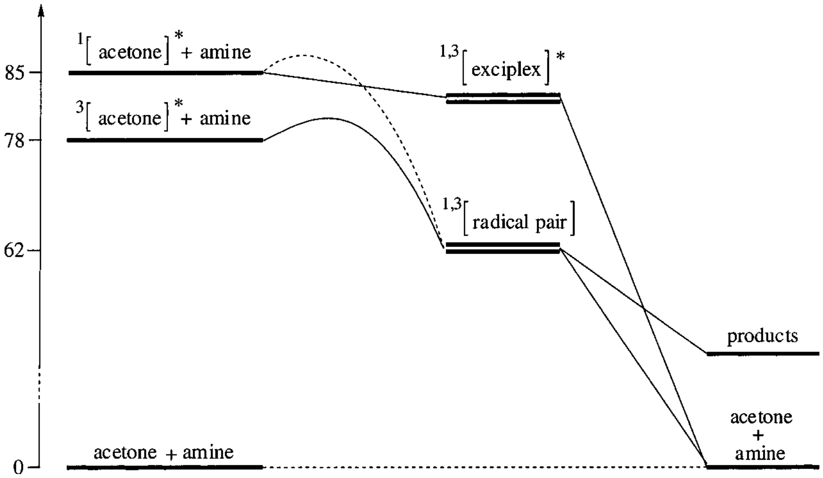
[94] Sadovskii, N. A.; Kuzmin, M. G.; Görner, H.; Schaffner, K. *Chem. Phys. Lett.* **1998**, *282*, 456−465.

[95] Kikuchi, K.; Takahashi, Y.; Katagiri, T.; Niwa, T.; Hoshi, M.; Miyashi, T. *Chem. Phys. Lett.* **1991**, *180*, 403−408.

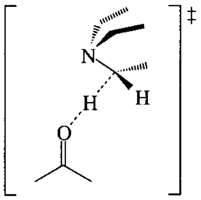
[96] For the application of the Kirkwood continuum model according to ref 23, the dipole moments of singlet-excited acetone (1.7 D), triethylamine (1.0 D), and the exciplex (4.2 D) were extracted from single-point CI calculations of UHF-PM3 optimized structures. The molecular radii for the reactants (acetone and triethylamine) are 2.78 and 3.44 Å respectively; cf.: Terazima, M.; Okamoto, K.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 13387−13393. The molecular radius of the exciplex was estimated by assuming volume additivity of the reactants (3.96 Å). With these data the structural constant *C* (as defined in ref 23) is calculated as −0.125 D$^2$ Å$^{-3}$, which falls between that of 2,3-diazabicyclo[2.2.2]oct-2-ene (0.101 D$^2$ Å$^{-3}$) and benzophenone (−0.466 D$^2$ Å$^{-3}$).

[97] Hubig, S. M.; Rathore, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 617−626.

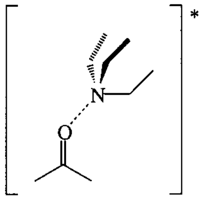
**Scheme 3**



abstraction from adjacent α C−H bonds needs to be considered. This reaction pathway is postulated for aromatic hydrogen donors.[9,10] However, we contend that this follow-up reaction is unlikely for amines.



**I**



**II**

We have recently analyzed the transition state for H abstraction (structure **I**), which requires a collinear arrangement of a C−H bond with the half-vacant n orbital of the excited state.[22,25] This transition-state geometry cannot be attained without loss of the exciplex stabilization, which requires the same n orbital to coordinate with the nitrogen lone pair (structure **II**). The two transition states **I** and **II** are too different to imagine a transition state that promotes H abstraction while maintaining the CT stabilization, especially since an efficient interaction with the nitrogen lone pair is crucial to facilitate C−H abstraction (stereoelectronic effect; see above). Indeed, no indication for exciplex-mediated H abstraction was obtained in high-level calculations.[20] The fact that this pathway does play a role for aromatic ketones and aromatic hydrogen donors is presumably due to the involvement of structurally very different $\pi$ exciplexes,[9,10] thus allowing the carbonyl group to access the reactive benzylic hydrogens without complete loss of the CT stabilization in the transition state.

**Thermodynamic Interpretation.** The combined data point to a pronounced switch-over in photochemical reaction mechanism from a rather pure H abstraction for triplet acetone to significant exciplex-induced quenching for the singlet-excited state. This results also in a pronounced change in selectivity, namely, preferential reaction with good electron donors for the singlet and good hydrogen donors for the triplet. A competition of two different photoreaction mechanisms was earlier proposed for biacetyl,[30] where, however, electron transfer becomes exergonic for both spin states.[31] In more detail, relative contributions of exciplex or contact ion pair formation and H abstraction have been discussed by Wagner et al.[9] and more recently by Coenjarts and Scaiano[10] for triplet aromatic ketones and alkylbenzenes in dependence on aryl substitution, which allows a variation of the redox potentials and excitation energies.

The sudden switch-over in reaction mechanism for acetone can be rationalized on the basis of simple thermodynamic arguments (Scheme 3). The reaction of excited acetone with triethylamine will be discussed as an example. For the sake of simplicity, we assume that the singlet−triplet energy splittings in the exciplex and radical pair are small, which is expected on the basis of the small exchange interaction in the radical pairs and the diradical-type exciplex structures.

The reaction enthalpy for the direct H abstraction process of the ground-state molecules can be estimated as 62 kcal mol$^{-1}$.[85] By using the excitation energies for singlet-excited (85 kcal mol$^{-1}$) and triplet acetone (78 kcal mol$^{-1}$), the reaction enthalpies for photoinduced H abstraction can be calculated. One obtains values of −23 kcal mol$^{-1}$ for singlet-excited acetone and −16 kcal mol$^{-1}$ for triplet acetone. Although electron transfer is energetically unfavorable (cf. Results), the formation of an exciplex can be slightly exothermic due to a stabilization by electronic coupling as proposed by Kuzmin.[93,94] This finding was verified for the quenching of n,$\pi$* singlet-excited 2,3-diazabicyclo[2.2.2]oct-2ene by amines, for which electron transfer is similarly improbable, but for which exciplex formation is slightly exothermic (~2 kcal mol$^{-1}$), as confirmed by high-level quantum-chemical calculations.[20]

The situation for the triplet-state reaction of acetone with triethylamine is clear-cut: Exciplex formation is expected to be an uphill process, while the direct H abstraction is downhill and prevails. At first glance, the situation is more complicated for the fluorescence quenching of acetone. Exciplex formation and the direct H abstraction are exothermic, but the thermodynamics favors the latter process. However, the experimental observations suggest that exciplex formation does compete and may actually dominate for tertiary amines. In fact, it is well known that photoinduced and radical-induced H abstractions have an intrinsic activation barrier.[3,22,98,99] In contrast, the exciplex can be formed in a diffusive equilibrium and may deactivate through a close-lying intersection in an essentially barrierless manner.[20] This interpretation is fully supported by the presently observed negative activation energies, which are

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(98) Johnston, H. S.; Parr, C. *J. Am. Chem. Soc.* **1963**, *85*, 2544−2551.

(99) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1667−1672.

inconsistent with a direct H abstraction but suggest the involvement of a singlet exciplex.

## Conclusions

Acetone is the simplest n,$\pi$*-excited ketone but displays a very interesting and diverse photochemistry. This has now been examined for amines, which are well known to display large structural and electronic effects on excited-state quenching. Most interestingly, the selectivity of singlet- and triplet-excited acetone toward amines differs notably, displaying a preference toward electron donors for the singlet and one toward hydrogen donors for the triplet. This points to a switch-over in reaction mechanism from a pure hydrogen abstraction for the triplet to competitive exciplex-induced quenching for the singlet. The latter quenching mechanism has been recently examined in detail for singlet-excited azoalkanes[20,23,24,26] and is now confirmed for singlet-excited acetone by negative activation energies and the observation of large steric effects on the quenching, which have been previously sought for.[42] While exciplex formation of singlet-excited acetone may involve varying degrees of charge transfer, depending on the amine, a full electron transfer can be excluded due to the very negative reduction potential of acetone and the lack of a solvent effect.

The reaction mechanism for triplet acetone involves a rather pure H abstraction as evidenced by the excellent correlation with the reaction rates of cumyloxyl radicals and the observation of stereoelectronic effects. The reaction rate constants for cumyloxyl radicals with amines measured in this study reveal the importance of a polar effect for this radical reaction. Consequently, the electron-donating abilities of the amines play a role in triplet quenching, but their importance does not exceed the effect observed for cumyloxyl radicals. While exciplex formation may compete for aromatic donors[11,62] and olefins as quenchers of triplet-excited acetone,[91] we suggest that it plays no significant role for amines. This is noteworthy since the quenching by amines as prototypal electron donors has almost always been associated with a significant degree of charge transfer. The experimental results, including the switch-over in reaction mechanism, can be rationalized by simple thermodynamic arguments, assuming that the H abstraction involves a significant intrinsic activation barrier, while singlet exciplex formation does not. This is in line with recent experimental and theoretical results.[20,22]

**Acknowledgment.** The generous support by the Schweizerischer Nationalfonds and the Fonds der Chemischen Industrie (Kekulé fellowship for U.P.) is acknowledged. We thank Prof. E. Haselbach (University of Fribourg) for a gift of amine **12**.

JA011212E