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Reactivity and Efficiency of Singlet- and Triplet-Excited States in Intermolecular Hydrogen Abstraction Reactions

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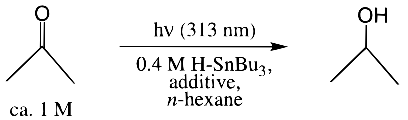
Abstract: The rate constants for quenching of the singlet- and triplet-excited state of acetone and a cyclic azoalkane by the hydrogen donors tributyltin hydride, 1,4-cyclohexadiene, and 2-propanol have been determined by time-resolved spectroscopy. It is concluded, in variance with previous studies, that singlet-excited states are significantly more reactive than triplet-excited states and that the reactivity difference between the two states of different spin multiplicity increases (*i*) with decreasing reactivity of the hydrogen donor and (*ii*) with increasing singlet−triplet energy gap of the excited state. This result is corroborated by semiempirical calculations. The relative efficiency for photoreduction by tributyltin hydride, which was determined by monitoring the formation of tributyltin radicals upon flash photolysis, was found to be four times lower for singlet-excited acetone than for the triplet state. The discrepancy between higher reactivity but lower efficiency in the intermolecular interaction of n,π*-excited singlet states with hydrogen donors is attributed to efficient radiationless deactivation, which has been predicted by correlation diagrams as a viable pathway for singlet-excited states.

Introduction

The photoreduction of ketones by alcohols was discovered nearly one century ago[1] and since then has become the most intensively studied photoreaction. Research has concentrated on understanding this intermolecular hydrogen abstraction by excited states mechanistically, and on using it for synthetic purposes.[2,3] Although it was recognized 60 years after its discovery that the triplet state acts as the primary reactive species,[4] the potential reactivity of the singlet-excited state in intermolecular hydrogen abstraction reactions has remained a standing concern.[2,5,6] Theory predicts comparable reactivity from both states[7−9] and one might further assume that the singlet-excited state is somewhat more reactive owing to its higher energy,[10,11] which is also expressed by *ab initio* calculations.[7] Experimental evidence, however, is also available for a significantly lower singlet reactivity. In particular, it has been claimed on the basis of the quantum yields for photoreduction and the absence of fluorescence intensity quenching that acetone and biacetyl singlets are significantly (ca. 10−100 times) less reactive toward tributyltin hydride than the triplet states.[12,13]

Scheme 1



1) additive = none $\Phi_R = 1.0$ Ref 12
2) additive = 5 M piperylene $\Phi_R < 0.01$ Ref 12
3) additive = 3 M 1-methylnaphthalene $\Phi_R = 0.07$ Ref 5

For example, the photoreduction of acetone by tributyltin hydride to yield 2-propanol proceeds with unit quantum yield (Φ_R) in the absence of triplet quenchers, but in the presence of triplet quenchers like piperylene[12] or 1-methylnaphthalene,[5] very little or no photoreduction reaction was observed, even at very high concentrations of tributyltin hydride (Scheme 1). From the quantum yields in the presence of triplet quenchers and given an intersystem crossing (ISC) rate constant of 5×10^8 M^{-1} s^{-1}, the effective rate constant for hydrogen abstraction by singlet acetone was first estimated[12] as $<10^6$ M^{-1} s^{-1} and later[5] as 1×10^8 M^{-1} s^{-1}, which is much lower than the value of 8×10^9 M^{-1} s^{-1} estimated for the triplet state. On the basis of these results, it was concluded that excited singlet acetone is appreciably less reactive than triplet acetone. While other aliphatic ketones are known for which the photoreduction of aliphatic ketones by tributyltin hydride is entirely suppressed by addition of the triplet quencher piperylene,[14] examples of photoreductions proceeding through the singlet state have also become available, but no rate data have been determined.[15]

In contrast to the reports that acetone fluorescence is not quenched by tributyltin hydride,[5] the fluorescence lifetime of 2-adamantanone was shortened by the same hydrogen donor with a quenching rate constant of 5×10^9 M^{-1} s^{-1}, which is only slightly lower than that assumed for triplet quenching of

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acetone (8×10^9 M^{-1} s^{-1}); unfortunately, no data for the adamantanone triplet state are available to allow a direct comparison and a firm conclusion to be drawn.[16]

With respect to less reactive hydrogen donors such as alcohols or alkanes, the singlet-excited state of acetone has been proposed to be quenched by 2-propanol with a rate constant similar to the triplet state.[17] This study, which again employed piperylene as quencher to eliminate triplet contributions, was in contrast to the assumed lower singlet reactivity toward the more reactive stannane. The data for the fluorescence quenching of adamantanone by alcohols indicated also a similar reactivity as for quenching of triplet acetone, but the order of rate constants correlated better with the ionization potentials of the alcohols than with the strength of their C−H bonds, indicating a possible participation of charge-transfer interactions.[5,16] The rate constants for fluorescence quenching of chloropentafluoroacetone by alkanes, however, followed the usual order of C−H bond strengths, and not their ionization potentials.[18]

Until today, no unambiguous conclusion has been reached on whether singlet or triplet states are more reactive toward intermolecular hydrogen donors.[2,5,6] To resolve experimentally this fundamental mechanistic aspect of photochemical reactivity, we have examined the quenching of the fluorescence lifetimes of acetone by the potent hydrogen donors tributyltin hydride and 1,4-cyclohexadiene, as well as by the less reactive 2-propanol. We find that singlet-excited acetone is 2−10 times more reactive than the triplet state. It is concluded, in agreement with the expectations expressed above but in variance with the earlier studies,[5,12,13,16] that the singlet state is significantly more reactive toward hydrogen donors. This finding is also supported by the reactivity of a singlet-excited cyclic azoalkane toward the same set of hydrogen donors, which is 30−150 times higher than for the corresponding triplet state. While the singlet-excited states are inherently more reactive toward hydrogen donors, the efficiency for photoreduction, i.e., the actual transfer of the hydrogen atom to the excited state, is lower than for the triplet. This result is explained with the correlation diagram for intermolecular hydrogen abstraction.[7,8]

Experimental Section

Acetone, acetonitrile, benzene, cyclohexane, 2-propanol, and *n*-pentane (BDH, Omnisolv grade), carbon tetrachloride (99.9%), tributyltin hydride (97%), tributyltin deuteride (97%), 1,4-cyclohexadiene (97%), and tetramethyltin (99%) were employed as received (Aldrich). Biacetyl (Aldrich) was distilled once prior to use. The cyclic azoalkane (IUPAC name: (*c*-4a,*c*-8a)-1,4,4a,5,6,7,8,8a-octahydro-10,10-dimethyl-*r*-1,*c*-4:*t*-5,*t*-8-dimethanophthalazine) was synthesized according to the literature procedure;[19] the sample was purified by column chromatography on silica gel (methylene chloride/methyl *tert*-butyl ether) and two subsequent sublimations. The viscosity measurements were performed with a 50/P34 Cannon-Fenske viscometer. The time-resolved studies were done in Suprasil quartz cells with 7-mm optical path. The measurement of the fluorescence intensity quenching was performed with acetone samples contained in 10-mm optical path fluorescence cells by employing a Perkin Elmer LS-50 luminescence spectrometer and excitation wavelengths between 260 and 310 nm. Optical absorption spectra were obtained with an HP-8451A diode array spectrophotometer. All samples were deaerated by bubbling oxygen-free nitrogen through the solution, except in the case of the fluorescence intensity quenching experiment for acetone, which was run under air, *cf.* $^1k_q(O_2) = 2.3 \pm 0.5 \times 10^9$ M^{-1} s^{-1}.[20] All measurements were done at room temperature.

A Continuum PY61-10 Nd-YAG laser system with the third or fourth harmonic for excitation at 266 or 355 nm (ca. 0.5 mJ per 30-ps pulse) and a Hamamatsu streak scope C4334 system with Hamamatsu software were used for time-resolved fluorescence detection and data acquisition. This technique allows one to obtain singlet lifetimes and real-time kinetic quenching data in the fluorescence time regime relevant for the examination of acetone and the azoalkane (ca. 0.1−10 ns). Front-face irradiation of the samples allowed the examination of quenchers with absorbance at the irradiation wavelength. Acetone was excited at 266 nm and the azoalkane and biacetyl at 355 nm. For the time-resolved fluorescence measurements, one set of experiments was carried out in acetone as solvent and fluorescer, while for the other experiments the acetone concentration was 0.2−0.3 M in 2-propanol or tetramethyltin. The azoalkane concentration was chosen as ca. 10 mM in benzene or 2-propanol. The absorbance of biacetyl in cyclohexane was adjusted to ca. 2.0 at 355 nm.

The nanosecond time-resolved laser flash photolysis technique available in our laboratory was employed to monitor the transient absorption and emission. The setup was similar to that described previously,[21] except that a Tektronix 2440 digitizer was used to capture the signals from the monochromator−photomultiplier system and the data acquisition was controlled by a PowerMacintosh computer customized with LabVIEW 3.1 software from National Instruments. Triplet lifetimes and triplet quenching rate constants were measured by employing excitation at 266 or 308 nm and time-resolved phosphorescence spectroscopy for acetone (at 450 nm) or by employing excitation at 355 nm and time-resolved transient absorption spectroscopy for the azoalkane (at 310 or 450 nm). The lasers employed were a Continuum Surelite Nd-YAG laser with the third or fourth harmonic at 266 or 355 nm (ca. 30 mJ per 6-ns pulse) and a Lumonics EX-530 excimer laser operated with a Xe/HCl/Ne gas mixture at 308 nm (ca. 80 mJ per 6-ns pulse). For the transient absorption experiments, the concentrations of acetone and azoalkane were 40 and 2 mM, respectively; for the time-resolved phosphorescence, 10 mM acetone solutions were chosen. In one laser flash experiment the formation of tributyltin radicals from acetone was monitored by their transient absorption at 390 nm. For this experiment, an excitation wavelength of 308 nm was selected, and the acetone concentration in tetramethyltin, acetonitrile, or tributyltin hydride was chosen to achieve an absorbance of 0.7 at the irradiation wavelength.

Results

The weak fluorescence of acetone (Φ_f ca. 0.001)[22] is readily observable with streak camera detection, and the effect of quenchers on the fluorescence lifetimes can be examined (Figure 1). Each experiment provides as well the fluorescence spectrum (Figure 1), which is important to rule out the observation of fluorescence from the quencher itself, impurities, or photoproducts. In order to establish possible fluorescence quenching by different solvents, the fluorescence lifetimes of acetone were determined (±5%) in acetone (1.81 ns), acetone-d_6 (2.30 ns), tetramethyltin (1.93 ns), acetonitrile (1.85 ns), 1,1,2-trichloro-1,2,2-trifluoroethane (1.96 ns), chloroform (2.07 ns), chloroform-*d* (2.06 ns), and 1,2-dibromoethane (2.05 ns). The lifetimes are all in the range of 1.9 ± 0.1 ns which precludes significant solvent quenching effects; nevertheless, acetone appears to be a weak self-quencher of its fluorescence. The observation of longer acetone singlet lifetimes in tetramethyltin and 1,2-dibromoethane relative to neat acetone as solvent demonstrates that an enhancement of intersystem crossing due to external heavy atom effects is insignificant, as expected for n,π*-excited ketones.[23] A heavy atom induced enhancement

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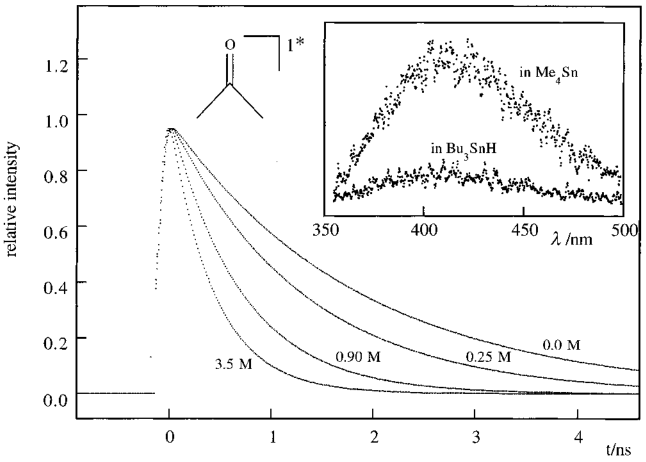


Figure 1. Decay of acetone fluorescence (0.2−0.3 M) in tetramethyltin at different concentrations of tributyltin hydride as quencher normalized to the same initial intensity; the decays correspond to first-order singlet lifetimes of 1.93, 1.29, 0.68, and 0.41 ns. Shown in the inset are the corresponding fluorescence spectra obtained in neat tetramethyltin and neat tributyltin hydride by integration of the photon count between 0 and 4 ns.

of ISC in tributyltin hydride is even less likely due to the two times lower concentration of tin atoms compared to tetramethyltin. Similarly, the acetone singlet lifetime in tetramethyltin demonstrates that hydrogen abstraction from the α (Sn)−C−H bonds is not significant.

The extinction coefficients at 266 nm in *n*-pentane solution (in cm^{-1} M^{-1}) were determined for acetone (12), tributyltin hydride (0.4), and tetramethyltin (0.1). Despite the low extinction coefficient of the organotin compounds sufficient acetone (0.2 M) was needed to ensure that most of the light was absorbed by the acetone even at very high stannane concentrations. Commercial tributyltin hydride showed weak fluorescence upon 266-nm excitation (λ_{max} = 325 nm), but it did not interfere in the region examined for acetone fluorescence (360−450 nm); moreover, this fluorescence, which may be due to an impurity in commercial tributyltin hydride, vanished on addition of 0.2 M acetone.

Acetone itself and tetramethyltin were chosen as suitable solvents for the fluorescence quenching experiments due to their complete miscibility with tributyltin hydride, which was a crucial requirement in view of the high quencher concentrations needed to achieve significant effects. Many other solvents (e.g., alkanes and acetonitrile) are not miscible at high stannane concentrations. Significant (>5%) quenching of the singlet lifetime was observed even at a 50 mM stannane concentration in acetone or tetramethyltin. The fluorescence decays (Figure 1) were cleanly first order at all quencher concentrations; the fluorescence intensity of acetone decreased considerably with increasing stannane concentration but the band contour and maximum was undisplaced at ca. 410 ± 5 nm (Figure 1), similar to the maximum wavelength observed in conventional fluorescence experiments (λ_{max} ca. 406 nm). From the initial slopes of the kinetic plots quenching rate constants of 8.1×10^8 M^{-1} s^{-1} in acetone and 1.04×10^9 M^{-1} s^{-1} in tetramethyltin (Figure 2a) were determined. The smaller value in acetone may in part be due to the fact that acetone functions as a self-quencher of its fluorescence, an effect that would diminish as its concentration decreases by addition of quencher.

At quencher concentrations larger than ca. 50% (≥1.8 M) the kinetic plots showed deviation from linearity, resulting in apparently lower quenching rate constants. In neat tributyltin hydride (ca. 3.5 M) the fluorescence lifetime was 0.41 ns, corresponding to ca. 78% singlet quenching or a quenching rate constant of ca. 5×10^8 M^{-1} s^{-1}. The curvature in the plots is attributed to the change in viscosity on going from neat acetone or tetramethyltin to neat tributyltin hydride as solvent. Indeed, the viscosities at room temperature were found to be 0.27 ± 0.03 cP for tetramethyltin but 1.1 ± 0.1 cP for tributyltin hydride with reference to the known viscosities (at 25 °C) of acetone (0.32 cP) and acetonitrile (0.35 cP). Among the two solvents, acetone and tetramethyltin, the latter proved to be the better solvent choice for acetone fluorescence quenching experiments since the acetone singlet lifetime was slightly longer than in acetone, and since the concentration of acetone could be kept constant in this three-component system. Thus, solvent-type changes were minimized when high concentrations of Bu_3SnH were used as reactant.

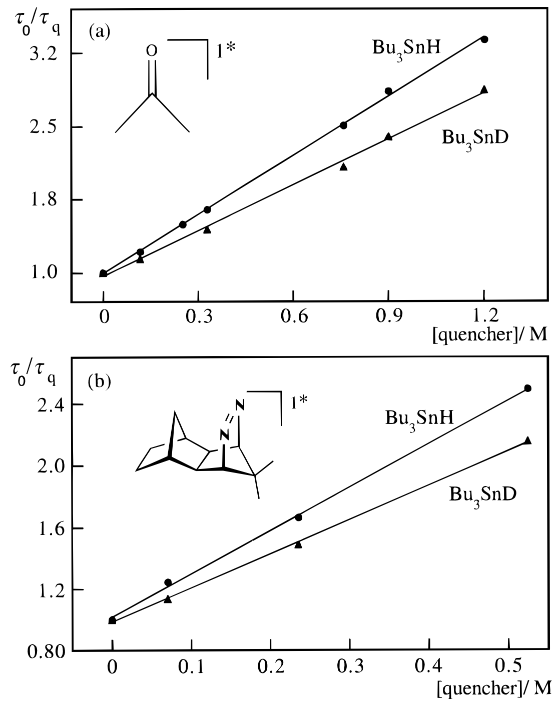
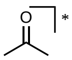
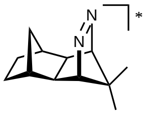


Figure 2. Plot of the ratios of the fluorescence lifetimes of acetone (a) and the cyclic azoalkane (b) in the absence (τ_0) and presence (τ_q) of the quenchers tributyltin hydride and deuteride as a function of their concentration.

In view of the rate constants obtained from the measurements of the fluorescence lifetimes of acetone as a function of stannane concentration (ca. 1×10^9 M^{-1} s^{-1}), earlier reports that the fluorescence intensity of acetone is not measurably quenched by this hydrogen donor require revision.^{5} Thus, it was important to establish the reasons for the failure to observe fluorescence quenching in conventional luminescence intensity experiments. Surprisingly, employing a fresh sample of tributyltin hydride and using *n*-pentane as solvent, fluorescence quenching was observed readily at excitation wavelengths ranging from 260 to 320 nm. The fluorescence quenching experiment yielded a Stern−Volmer slope of 2.3 ± 0.2 M^{-1}, from which a quenching rate constant of $1.2 \pm 0.2 \times 10^9$ M^{-1} s^{-1} was obtained (using $^1\tau_0 = 1.9 \pm 0.1$ ns). This value is in excellent agreement with the estimate from the time-resolved experiments and renders the high reactivity of acetone singlets toward tributyltin hydride a reproducible experimental fact. Moreover, the consistency of the time-resolved and steady state fluorescence quenching data rules out the (highly unlikely) possibility that the shortening of the fluorescence lifetimes by tributyltin hydride is due to an enhancement of the emission rate constant.

The rate constant for fluorescence quenching of biacetyl by

Table 1. Rate Constants for Quenching of the Singlet ($^{1}k_q$) and Triplet ($^{3}k_q$) n,π* States of Acetone and of a Cyclic Azoalkane by Hydrogen Donors (in M^{-1} s^{-1})

	 ΔE_{ST} = 7 kcal/mol		 ΔE_{ST} = 16 kcal/mol	
quencher	$^{1}k_q$[a] singlet-excited	3k_q[b] triplet-excited	$^{1}k_q$[c] singlet-excited	$^{3}k_q$[d] triplet-excited
tributyltin hydride	1.0×10^{9}	5.4×10^{8}	9.8×10^{8}	3.5×10^{7} [e]
1,4-cyclohexadiene	2.1×10^{8}	6.3×10^{7}	9.5×10^{8}	2.4×10^{7} [f]
2-propanol	9.1×10^{6} [g]	1.0×10^{6} [h]	8.9×10^{7} [g]	$\leq 6.4 \times 10^{5}$ [g,i]

[a] From fluorescence lifetimes in tetramethyltin; error ±10%. [b] From phosphorescence lifetimes in acetonitrile; error ±15%. [c] From fluorescence lifetimes in benzene; error ±10%. [d] From T−T transient absorption lifetimes; error ±15%. [e] In benzene. [f] In carbon tetrachloride. [g] From excited state lifetime in neat 2-propanol. [h] References 16 and 27. [i] See text.

tributyltin hydride was also determined by measuring the effects on the fluorescence lifetimes upon 355-nm picosecond laser excitation ($^{1}\tau_0 = 11.4 \pm 0.3$ ns in cyclohexane). The value obtained (2.7×10^{7} M^{-1} s^{-1}, three data points) was again significantly higher than that previously reported ($<3 \times 10^{6}$ M^{-1} s^{-1}),[13] which was based on steady state techniques.

A kinetic isotope effect of 1.28 was determined for the quenching of the acetone fluorescence lifetimes by the stannane in tetramethyltin as solvent (Figure 2a). The observed kinetic isotope effect establishes an interaction with the Sn−H bond as the quenching mechanism. The relatively low isotope effect is in accordance with the high quenching rate constant and agrees with the inherently smaller deuterium isotope effect expected for stannanes [$\tilde{\nu}$(Sn−H) ≈ 1820 cm^{-1}, corresponding to a maximum kinetic deuterium isotope effect of ca. 3.6]. It is also a general observation that kinetic isotope effects in most photochemical hydrogen abstraction reactions fall short of the theoretical maximum values.[24] Moreover, since the reactivity of excited ketones is often compared with that of alkoxy radicals, it is important to recall that the kinetic isotope effect for the hydrogen abstraction of *tert*-butoxy radicals from tributyltin hydride (1.23) is similar to the presently observed value.[25]

The fluorescence quenching rate constant for acetone was also determined for 1,4-cyclohexadiene as quencher in tetramethyltin by means of a kinetic plot at several quencher concentrations and a value of 2.1×10^{8} M^{-1} s^{-1} was obtained. For 2-propanol the rate constant of 9.1×10^{6} M^{-1} s^{-1} was determined from the lifetime in the neat quencher ($^{1}\tau_0 = 1.55$ ns) relative to other solvents ($^{1}\tau_0 = 1.9 \pm 0.1$ ns). This value specifies an earlier estimate for the rate constant of hydrogen abstraction by singlet acetone from 2-propanol; the latter was subject to a large error limit ($0.24-2.8 \times 10^{7}$ M^{-1} s^{-1}), but is now found to be of the right order of magnitude.[17] All data are collected in Table 1, which contains the fluorescence quenching rate constants for the cyclic azoalkane as well. The latter were also determined by kinetic plots at four different quencher concentrations for tributyltin hydride in benzene ($^{1}\tau_0 = 2.8$ ns) and for 1,4-cyclohexadiene in carbon tetrachloride ($^{1}\tau_0 = 4.1$ ns), and by using the lifetime in neat 2-propanol ($^{1}\tau_0 = 0.71$ ns) relative to carbon tetrachloride. The rate constant for quenching by tributyltin hydride was again found to be ca. 1×10^{9} M^{-1} s^{-1} (Figure 2b) as for acetone and a similar deuterium isotope effect was observed (1.27), which implies that the quenching mechanism is the same for both singlet-excited chromophores.[26]

The quenching rate constants for triplet acetone were determined in acetonitrile as the solvent by monitoring the phosphorescence lifetimes as a function of quencher concentration (Table 1); the value for 2-propanol was taken from the literature.[16,27] The quenching rate constant obtained for tributyltin hydride (5.4×10^{8} M^{-1} s^{-1}) is somewhat lower than the value previously estimated from product studies in *n*-hexane (8×10^{8} M^{-1} s^{-1}).[12a] As noted earlier,[28] the assumed diffusion rate constant to obtain the latter value appears to be too high, rendering the previous value as an upper limit. The present rate constant for quenching of triplet acetone also compares better with the values of 2.9×10^{8} M^{-1} s^{-1} for triplet benzophenone and 1.9×10^{8} M^{-1} s^{-1} for *tert*-butoxy radicals.[25]

The cyclic azoalkane examined is a member of the class displaying long-lived T−T absorption and phosphorescence.[29] As a consequence, the quenching rate constants for the triplet state of this azoalkane, which present the first rate constants for quenching of an azoalkane triplet state by hydrogen donors, could be determined from the triplet lifetimes as a function of quencher concentration. Benzene was used as a solvent in the case of tributyltin hydride and carbon tetrachloride in the case of 1,4-cyclohexadiene. The triplet lifetimes in these solvents in the absence of quenchers ($^{3}\tau_0$) are 620 and 580 ns, respectively. For 2-propanol, the rate constant was estimated by comparing the triplet lifetime in neat 2-propanol ($\tau_0 = 100$ ns) with that in carbon tetrachloride ($^{3}\tau_0 = 630$ ns). It cannot be decided whether the lifetime shortening in 2-propanol is due to hydrogen abstraction or a polar effect, since the triplet lifetime in a 1/1 water−acetonitrile mixture (115 ns), a solvent mixture with poor hydrogen donating properties, is very similar to that in 2-propanol. Moreover, while the lifetime in methanol is 230 ns, no deuterium isotope effect was observed, which again favors a polar effect rather than hydrogen abstraction. Hence, the rate constant for quenching of the triplet azoalkane by 2-propanol (Table 1) constitutes an upper limit for the actual rate constant of quenching due to interaction with the C−H bond and the ratio of rate constants due to quenching of the singlet- and triplet-excited azoalkane (Table 2) should be regarded as a lower limit.

The relative yields of tributyltin radicals obtained immediately after the quenching of excited acetone were determined in flash

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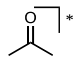
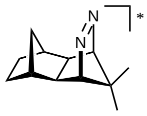
Table 2. Experimental[a] and Calculated[b,c] Ratios of Rate Constants for Singlet and Triplet Quenching of Acetone and a Cyclic Azoalkane

				
	$^1k_q/^3k_q$		$^1k_q/^3k_q$	
quencher	exptl	calcd	exptl	calcd
tributyltin hydride	1.9	2.5	28	12
1,4-cyclohexadiene	3.3	2.7	40	92
2-propanol	9.1	16.1	$\geq 140^c$	10^7

[a] From Table 1. [b] The semiempirical Bond-Energy-Bond-Order method was employed. [c] See text.

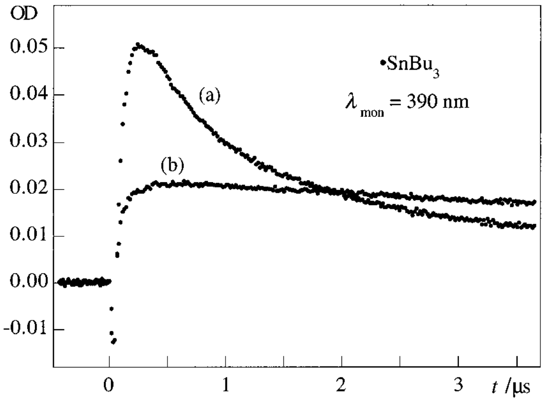


Figure 3. Pair of transient absorption decay traces obtained on flash photolysis (λ_{exc} = 308 nm, λ_{mon} = 390 nm) of samples containing acetone (OD = 0.70) in (a) tetramethyltin with 18 mM tributyltin hydride and (b) in neat tributyltin hydride (3.5 M). The emission and the initial growth are attributed to the response of the photomultiplier to the fluorescence of acetone, while the transient absorption is assigned to tributyltin radicals produced from hydrogen abstraction by excited acetone. The slower decay in tributyltin hydride as solvent is attributed to its higher viscosity.

photolysis experiments by measuring the absorbance at 390 nm, the absorption maximum of tributyltin radicals.[25] In a representative set of experiments (Figure 3), two optically matched solutions of acetone (OD_{308} = 0.70), one in tetramethyltin with 18 mM tributyltin hydride, the other in neat tributyltin hydride (3.7 M), were photolyzed at 308 nm using identical laser pulse intensities. The sample in tetramethyltin with 18 mM stannane produced a maximum transient absorption of 0.051 at 390 nm, while the sample in neat stannane yielded a value of 0.021. Irradiation of neat tributyltin hydride at 308 nm (without additive) also yielded a small absorbance in this region (ca. 0.005), but this contribution was found to be negligible (<5%) in view of the large absorbance of acetone employed in the actual experiment (0.7 *versus* ca. 0.05). In a control experiment with acetonitrile and 18 mM stannane, the same absorbance at 390 nm was observed, which implies that the radical yield is approximately the same as in tetramethyltin. The transient decayed by clean second-order kinetics (radical recombination), and by using the known extinction coefficient[25] $\epsilon_{max} = 450\ M^{-1}\ cm^{-1}$ the second-order rate constants ($2k_t$) were estimated as ca. $8 \times 10^8\ M^{-1}\ s^{-1}$ in tributyltin hydride and ca. $5 \times 10^9\ M^{-1}\ s^{-1}$ in tetramethyltin and acetonitrile. The significantly lower rate constant in tributyltin hydride is not surprising in view of its 3−4 times higher viscosity (see above).

In the samples containing 18 mM stannane, only 3% of the singlets are expected to be intercepted by the stannane, while >96% of the triplets are expected to be quenched ($^3\tau_0 = 2.5\ \mu s$ in tetramethyltin and $^3\tau_0 > 15\ \mu s$ in acetonitrile). Thus, since the photoreduction of acetone triplets by stannane proceeds with unit quantum efficiency,[12a] the 390-nm absorbance measured for this solution (0.051) was taken as a 100% yield of tributyltin radicals. In contrast, since the singlet lifetime in neat stannane is 0.41 ns *versus* 1.9 ns in acetonitrile or tetramethyltin, ca. 78% of the singlets are quenched, and the remaining 22% undergo ISC to the triplet state to be quantitatively quenched subsequently. Hence, a fraction of the 390-nm absorbance measured in neat quencher corresponds to the triplet reaction, and the contribution can be evaluated from the 100% value obtained in the dilute solution, which provides a transient absorbance triplet contribution of $0.22 \times 0.051 = 0.011$. Subtracting this fraction attributable to the triplet pathway from the absorbance obtained in neat tributyltin hydride provides an absorbance value of $0.021 - 0.011 = 0.010$, which derives from the quenching of 78% acetone singlet states.

The comparison of the absorbance characteristic for triplet state quenching with the corrected value for singlet quenching gives an efficiency of only 25% for tributyltin radical formation, i.e., photoreduction, resulting from quenching of singlet-excited acetone by tributyltin hydride. The remaining 75% of the quenching processes are assumed to return to the ground state molecules, i.e., $\phi_r = 0.25$ and $\phi_d = 0.75$. This quantification relies on the reasonable assumption that the extinction coefficient of tributyltin radicals is the same in the selected solvents, which is also supported by the observation that the transient absorbances at 390 nm were the same in acetonitrile and tetramethyltin, each containing 18 mM tributyltin hydride (see above).

An attempt was made to measure the quantum yields for acetone photoreaction at 308 nm as a function of tributyltin hydride concentration in order to obtain experimental information on radiationless deactivation processes; a decrease of the quantum yield is expected at high quencher concentrations, if singlet quenching was mainly due to radiationless deactivation, which is implied by the observation of reduced tributyltin radical formation from the singlet (see above). Unfortunately, such measurements proved to be difficult at the required high concentrations of tributyltin hydride, since formation of photoproducts occurred in the same region as the absorbance of acetone. Thus, although the absorbance remained initially constant upon 308-nm irradiation (a similar observation was made by Wagner in the presence of high stannane and piperylene concentration),[12a] it was not clear to which degree this effect was due to formation of absorbing products or to a reduced acetone depletion. This limitation, along with the described thermal reaction of acetone with the stannane,[12a] precluded reliable experimental information on radiationless deactivation by means of UV spectral data.

The semiempirical bond-energy−bond-order method[10,28,30] was employed to calculate the expected differences in reactivities (ratios of quenching rate constants) for the singlet- and triplet-excited states of acetone and the cyclic azoalkane. The method requires thermodynamic parameters and bond lengths as input data. For acetone and the hydrogen donors the required data were taken to be the same as in the earlier work[10,28,30] and from the literature.[31] For the cyclic azoalkane the data were estimated from the available parameters for hydrazine and its derivatives and from other azoalkanes.[32] The bond dissociation energies were taken as (in kcal/mol) N−H = 80, C−N = 83, and Sn−N

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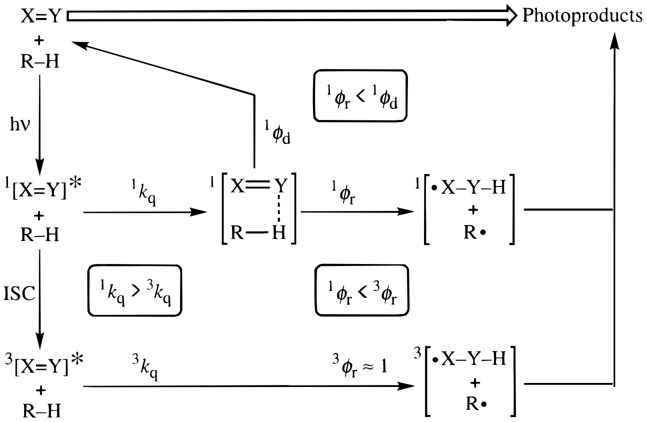
(30) (a) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin. Trans. 2* **1975**, 934. (b) Johnston, H. S.; Parr, C. *J. Am. Chem. Soc.* **1963**, *85*, 2544. (c) Zavitsas, A. A.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645.

(31) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218.

(32) (a) Schmidt, E. W. In *Hydrazine and its Derivatives*; Wiley: New York, 1984; pp 232−327. (b) Winter, N. W.; Pitzer, R. M. *J. Phys. Chem.* **1975**, *62*, 1269.

Scheme 2



= 75 and the bond lengths employed were 1.04 Å for N−H and 1.47 Å for C−N. The strength of the π bond in azoalkanes was assumed as 60 kcal/mol,[32b] and the triplet energy for the cyclic azoalkane is known accurately (63 kcal/mol).[29] As proposed previously,[30a] the second-order repulsion potential was approximated as 10% of the first-order repulsion. Conversely, for the singlet-excited states the second-order potential was assumed to be *attractive* [10] and was subtracted (10%) from the first-order repulsive potential.

The bond-energy−bond-order method provides activation energies (V^*) and preexponential factors (B) for a rate expression that resembles the Arrhenius equation: $k = Be^{-V^*/RT}$. It was assumed for the calculation of the ratio of the rate constants that the preexponential factors (B) are the same for the singlet and triplet reaction with a particular hydrogen donor, i.e., $^1k_q/^3k_q = e^{\Delta V^*/RT}$, where ΔV^* was the difference in the calculated activation energies. The calculated ratios for the singlet and triplet quenching rate constants are compared in Table 2 with the experimental data. All photoreactions were calculated to be exothermic except for the triplet reaction of the azoalkane with 2-propanol, which was 9 kcal/mol endothermic.

Discussion

When discussing rate constants of intermolecular photochemical processes, it is important to differentiate between absolute rate constants for quenching of the excited states (k_q) and effective rate constants for formation of photoproducts (k_r). The former describe primary photochemical reactivity and the latter are obtained by multiplication of the quenching rate constants with the corresponding efficiency of the photoreaction ($k_r = \phi_r k_q$), i.e., they take into account the photoreaction quantum yield. Only for photoreactions with unit efficiency does k_q coincide with k_r. The presently discussed interactions of n,π^*-excited singlet and triplet states (X = Y) with hydrogen donors (R−H) are generalized in Scheme 2, which already contains the most important conclusions of our study. ϕ_d is the efficiency for deactivation of the singlet-excited state to replenish the reactants, which may occur from an excited complex (*vide infra*). Based on the situation in Scheme 2, the relative reactivity toward hydrogen donors equals $^1k_q/^3k_q$, where the superscripts denote the spin multiplicity of the excited state, and the relative efficiency of photoreduction equals $^1\phi_r/^3\phi_r$.

The relative reactivity and the relative efficiency of singlet- and triplet-excited n,π^* states in hydrogen abstraction reactions have been the subject of several discussions but no consistent conclusion has been reached. Since most studies have focused on acetone as the prototypal ketone we have examined this reaction in further detail with respect to both the relative reactivity and the relative efficiency. In addition, we have examined the quenching of a singlet- and triplet-excited azoalkane as an example for another n,π^* state. The quenching rate constants, which provide information on the reactivity toward the hydrogen donors, are shown in Table 1.

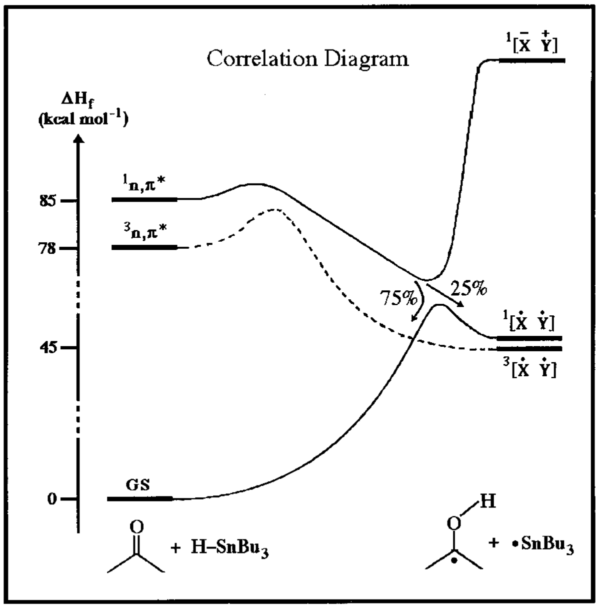


Figure 4. Correlation diagram for the intermolecular hydrogen abstraction by acetone from tributyltin hydride modified to reflect the lower activation energy of the singlet reaction.

The fluorescence quenching rate constant for acetone by tributyltin hydride has been determined in three different solvents by time-resolved and steady-state techniques to provide a value of ca. 1.0×10^9 M^{-1} s^{-1}; this value is ca. two times higher than the value for the quenching of the acetone triplet state by tributyltin hydride (5.4×10^8 M^{-1} s^{-1}). A significantly higher reactivity of singlet acetone is also observed for 1,4-cyclohexadiene and 2-propanol (factors 3 and 10). The combined results from Table 1 establish a much higher reactivity of ketone singlets than previously stipulated; in particular, they refute the notion that the intermolecular singlet reactivity toward hydrogen donors is reduced[5,12,13] or equal[16] compared to the triplet reactivity. The higher singlet reactivity toward hydrogen donors can be accounted for on thermodynamic grounds as shown in Figure 4 for tributyltin hydride as hydrogen donor; the heat of reaction was assumed to be −33 kcal mol^{-1} for the triplet reaction[30a] and the singlet−triplet energy gap was taken as 7 kcal mol^{-1}. The energy of the product radical pairs should be approximately the same for the triplet and singlet states, such that the singlet reaction is more exothermic owing to the higher energy of the singlet-excited states. This should result in lower activation energies for hydrogen abstraction, *cf.* Figure 4, which may account for the enhanced singlet reactivity. The observed higher reactivity of singlet-excited states resolves the previously recognized discrepancy[5] between intermolecular hydrogen abstraction reactions and Norrish-type II reactions, their intramolecular analog. In particular, the observed higher singlet reactivity for acetone corresponds with previous experimental results for the Norrish-type II reaction of 2-pentanones and 2-hexanones, for which the singlets were also found to be 2−25 times more reactive than the triplet states.[33]

We propose that the higher reactivity of singlet-excited states is not only characteristic for ketones, but general for all n,π^*-

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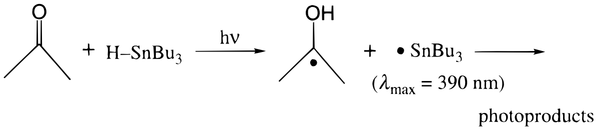
[33] (a) Formosinho, S. J.; Arnaut, L. G. *Adv. Photochem.* **1991**, *16*, 67, see table on p 100. (b) Encina, M. V.; Lissi, E. A. *J. Photochem.* **1976**, *6*, 173. (c) Encina, M. V.; Nogales, A.; Lissi, E. A. *J. Photochem.* **1975**, *4*, 75.

excited states, whose high reactivity toward hydrogen donors is inherently related to their electronic configuration. This is corroborated by the results for the cyclic azoalkane[29] shown in Table 1, which reveal a 30−150-fold singlet reactivity toward the same set of hydrogen donors. The steeper rise in reactivity for the azoalkane compared to acetone is surprising but one must recall that the singlet−triplet energy gap (ΔE_{ST}) for this azoalkane (16 kcal/mol)[29] is more than twice that for acetone (7 kcal/mol), which causes a larger difference in the activation energies for hydrogen abstraction from the singlet and triplet state. Finally, the presently determined rate constant for singlet quenching of biacetyl by tributyltin hydride (2.7×10^7 M^{-1} s^{-1}) appears to be somewhat higher than that for triplet quenching (1.5×10^7 M^{-1} s^{-1}).[13]

Lower activation energies for the singlet reaction have been predicted by early *ab initio* calculations.[7] The calculated difference in transition state energy for the hydrogen abstraction of singlet- and triplet-excited formaldehyde from methane was 10 kcal mol^{-1}. The data for acetone from Table 1 reveal a factor of 2−10 difference in the experimental rate data which would only correspond to a variation of 0.4−1.4 kcal/mol in the activation energies when the same preexponential *A* factors are assumed. Although additional computational studies have later appeared on the geometrical requirements and energetics for hydrogen abstraction by *triplet-excited* states,[8,34] little computational progress has been made with respect to the singlet reaction, and the comparison of singlet and triplet reaction. Hence, it cannot be judged whether the discrepancies between the calculated activation energy difference[7] and those implied by the present results are due to the simplicity of the STO-3G basis set used in the early calculations.[7] In addition, the discrepancy between the computed and experimental activation energy difference might reflect earlier transition states for the more reactive hydrogen donors in Table 1 compared to methane; the latter was used as a model for a hydrogen donor in the calculation.[7]

The semiempirical bond-energy−bond-order method[10,28,30] provides a readily accessible tool to evaluate changes in activation energies of hydrogen abstraction reactions and was used to evaluate the expected differences in singlet and triplet reactivity for acetone and the cyclic azoalkane. As can be seen from the experimental and calculated ratios of the singlet and triplet quenching rate constants (Table 2), the results of the semiempirical method, which uses bond dissociation energies and bond lengths as input parameters, are in good agreement with experiment. In particular, the calculated values suggest the same trend with hydrogen donors, i.e., the difference between singlet and triplet reactivity increases on going to less reactive hydrogen donors, and they reveal the observed trend with excited state energies, i.e., the difference between singlet and triplet reactivity increases on going to compounds with larger singlet−triplet energy gap (azoalkanes). Moreover, the method predicts the same order of magnitude in reactivity difference as experimentally observed, except for the interaction of the azoalkane with 2-propanol, where the experimental ratio should be considered as a lower limit, since it is not clear whether the slight quenching of the triplet state by 2-propanol is due to an interaction with the C−H bond.

While the quenching rate constants of hydrogen donors can be directly determined, the quantification of the effective rate constants for photoreduction requires knowledge of the efficiency of the photoreaction. In the case of the photoreduction of acetone by tributyltin hydride, the primary process leads to formation of ketyl and tributyltin radicals (eq 1). Thus, the efficiency of the photoreduction can be monitored by the amount of tributyltin radicals formed initially after flash photolysis.[35] Such experiments were carried out at medium and very high stannane concentrations to avoid or to maximize the participation of singlet photochemistry (Figure 3). The quantitative analysis of the data (*cf*. Results) reveals that the singlet-excited state of acetone is ca. four times *less* efficient in producing tributyltin radicals than triplet acetone. Since the quantum yield for photoreduction of acetone by tributyltin hydride has been found to be unity,[12a] the efficiency of photoreduction of singlet acetone (ϕ_r) is only 25% and the effective rate constant for photoreduction ^1k_r is only $0.25 \times {}^1k_q \approx 2.5 \times 10^8$ M^{-1} s^{-1}, i.e., it is lower than the effective rate constant for photoreduction of triplet acetone since $^3k_r = {}^3k_q = 5.4 \times 10^8$ M^{-1} s^{-1}. The remainder of acetone singlets, which do not undergo photoreduction, is required to undergo radiationless deactivation back to the ground-state reactants as depicted in Scheme 2, i.e., $\phi_d = 0.75$. The experiment employed to assess the efficiency of photoreduction by monitoring the formation of tin radicals (Figure 3) provides spectroscopic evidence for such deactivation processes and allows one to estimate the effective rate constant for deactivation of singlet acetone as $\phi_d k_q = 7.5 \times 10^8$ M^{-1} s^{-1}.



(1)

The low efficiency of hydrogen abstraction by singlet-excited acetone accounts for the experimental observation and apparent contradiction described by Wagner that the quantum yields for photoreduction as determined by product studies (2-propanol formation or ketone depletion) decrease from unity to very low values (≤7%) when the triplet reaction is suppressed by addition of triplet quenchers (Scheme 1).[5,12,13] This effect was observed at high stannane concentrations (0.4 M), which should have caused significant (ca. 43%) quenching of the more reactive singlets according to the quenching rate constant of 1×10^9 M^{-1} s^{-1} determined herein. Since the measured quantum yield is 7% in the case of the experiment involving 1-methylnaphthalene, the efficiency for photoreduction from the singlet state is 7%/43% = 16%, which compares reasonably well with the 25% efficiency derived from the spectroscopic method; conversely, the effective rate constant for photoreduction derived from these values (1.6×10^8 M^{-1} s^{-1}) agrees well with the spectroscopic estimate (2.5×10^8 M^{-1} s^{-1}). The quantum yield obtained from the experiment involving piperylene as triplet quencher (Scheme 1) appears to be too low, and indeed, it has been suggested that dienes may have adverse effects and annihilate the singlet photoreduction by abstracting hydrogen from the intermediary ketyl radicals to regenerate acetone.[5,16] Note that the previous product studies did not provide accurate

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(34) (a) Sengupta, D.; Sumathi, R.; Chandra, A. K. *New J. Chem.* **1991**, *15*, 901. (b) Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508. (c) Severance, D.; Morrison, H. *Chem. Phys. Lett.* **1989**, *163*, 545. (d) Severance, D.; Pandey, B.; Morrison, H. *J. Am. Chem. Soc.* **1987**, *109*, 3231. (e) For the Norrish-type II reaction see: Sauers, R. R.; Edberg, L. A. *J. Org. Chem.* **1994**, *59*, 7061. Sengupta, D.; Sumathi, R.; Chandra, A. K. *J. Photochem. Photobiol. A: Chem.* **1991**, *60*, 149.

(35) Note that under the high radical concentrations produced on laser flash photolysis, the major fate of the radicals will be recombination as revealed by the observed second-order decay. Under the low radical concentrations produced during conventional lamp irradiation for preparative purposes,[12a] however, the intermediary ketyl radical may further abstract a hydrogen atom from a second stannane molecule to form directly the photoreduction product 2-propanol, *cf*.: Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

information on the reactivity and efficiency of the singlet photoreduction, but allowed only an estimate of the lower limit for singlet reactivity. For example, it could not be previously decided whether singlet photoreduction is inherently less efficient or due to a lower quenching rate constant.

While hydrogen-abstraction–back-abstraction from the radical pair stage is one possible explanation for such deactivation of singlet states, it may also occur earlier on the reaction surface as exposed by the correlation diagram in Figure 4.[7,8] In the latter case return to the reactants occurs from an avoided crossing before the radical pair is reached, and we tentatively favor this explanation for radiationless deactivation of singlet-excited states by hydrogen donors. The correlation diagram in Figure 4 represents our present view of the interaction of excited acetone with tributyltin hydride, namely it reflects the lower activation energy for the singlet reaction, and shows the assumed fraction of singlet encounters proceeding to the radical pair (ca. 25%) or returning to the reactants (ca. 75%). Note that the reaction surface for the hydrogen abstraction by *triplet* acetone does not allow such deactivation due to the different spin multiplicities, but proceeds straight to the primary photoproducts (radical pair), as implied by the measured unit quantum yield for photoreduction.[12a] Although the implications of the correlation diagram for intermolecular hydrogen abstraction have been extensively discussed with respect to a possibly lower efficiency of the singlet reaction,[3,5,7,8,16,24,34a] we contend that the discrepancy between reactivity and efficiency for the intermolecular photoreduction of singlet- and triplet-excited states has not been rigorously established previously. Moreover, the observed lower efficiency of the singlet-excited state in the intermolecular reaction is in line with the previously proposed lower singlet efficiency in the Norrish-type II reaction of 2-hexanones.[36] This happenstance allows us to unify the view of photoinduced hydrogen abstraction reactions, which has been previously disturbed by the apparent variance between the inter- and intramolecular examples.

The question arises which factors determine the partitioning of the singlet quenching into chemical reaction and deactivation. In view of Figure 4, one might tentatively suggest that the slopes of the lowest singlet surface on each side of the avoided crossing are relevant. This would be the case if the minimum at the avoided crossing corresponds to an excited complex, which causes the system to pause at this point and later undergo a diabatic passage to the ground state surface.[8c] If this should be a viable explanation, two general expectations for the quenching of singlet-excited states by hydrogen donors can be expressed: (i) Since the ground-state molecules lie energetically below the radical pair, the slope in the direction of the reactants will always be steeper, thus favoring deactivation over chemical reaction. (ii) The ratio of the slopes will be more in favor of radiationless deactivation on going to less exothermic photoreductions, i.e., hydrogen donors with stronger bonds, and when the reaction becomes thermoneutral or endothermic, radiationless deactivation will proceed with unit efficiency. For singlet-excited ketones, in particular, one might expect that the fraction of chemical reaction does not exceed 25%, since this value is reached for the prototype of a particularly exothermic photoreduction (acetone/tributyltin hydride).[30a] A remarkable facet of these expectations is that the interaction of singlets with hydrogen donors remains no longer a chemical reaction but becomes a physical quenching mechanism, where the hydrogen donor causes deactivation by accepting part of the electronic excitation energy as vibrational energy and promoting internal conversion from S_1 to S_0.

The conclusion from the presently reported rate data in Tables 1 and 2 is simple and entirely intuitive: The higher the energy of an excited singlet relative to the triplet state the higher the intermolecular reactivity toward hydrogen donors. The differences in the singlet and triplet reactivity correlate with the magnitude of the quenching rate constants, which confirms the notion that higher reactivity results in lower selectivity, i.e., the reactivity difference between singlet and triplet state increases when the reaction becomes more endothermic. This result is correctly reproduced by semiempirical calculations. The observation that the efficiency of photoreduction of singlet-excited states, even for the comparably exothermic hydrogen abstraction of singlet-excited acetone and tributyltin hydride, is much lower than for the triplet reaction can be reconciled with the correlation diagram for hydrogen abstraction, which provides a possible pathway for radiationless deactivation by means of an avoided crossing to the lowest singlet surface. We contend that the efficient deactivation of singlet-excited states by hydrogen donors is a general photochemical phenomenon and hope to expose more experimental manifestations of this singlet quenching mechanism in the near future.

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(36) (a) Yang, N. C.; Elliot, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 7550. (b) Yang, N. C.; Elliot, S. P.; Kim, B. *J. Am. Chem. Soc.* **1969**, *91*, 7551. (c) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.