Evidence for Comparable Reactivity of Alkanone Excited Singlet and Triplet States toward Hydrogen Donors

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Abstract: Studies of solvent effects on the relative fluorescence quantum yield ($\phi_{fl}$) and fluorescence lifetime ($\tau_f$) of 2-adamantanone are presented. The ability of a given solvent to quench adamantane fluorescence correlates well with the facility of the solvent as a hydrogen donor, suggesting that the quenching process involves at least partial intermolecular hydrogen abstraction by the adamantane excited singlet state. Kinetic studies indicate that the alkanone $n,\pi^*$ singlet is just as reactive as the $n,\pi^*$ triplet toward quenching by hydrogen donors.

The intermolecular photoreduction of alky ketones has been the subject of considerable interest over the past few years. Particular emphasis has been placed on the importance of the multiplicity of the alkanone excited states ($S_1$ or $T_1$) and the degree of ring strain present in cyclic alkanones in determining the reactivity toward intermolecular hydrogen abstraction. It has been reported that the alkanone $n,\pi^*$ singlet state ($S_1$) is at least two or three orders of magnitude less reactive than the $n,\pi^*$ triplet state ($T_1$) toward intermolecular hydrogen abstraction. This result requires significant differences in the effect of excited-state multiplicity on intermolecular hydrogen abstraction and intramolecular hydrogen abstraction, for which the alkanone $S_1$ and $T_1$ states have been shown to have comparable reactivity.

We would like to present evidence from studies of solvent effects on the quantum yield and lifetimes of fluorescence from 2-adamantanone that demonstrate that several hydrogen donors quench the $n,\pi^*$ singlet and $n,\pi^*$ triplet states at equivalent rates. Our results suggest that alkanone $S_1$ and $T_1$ states have comparable reactivity (but not necessarily efficiency) toward intermolecular hydrogen abstraction.

Experimental Section

Solvents were at least spectral grade further purified by fractional distillation prior to use. 2-Adamantanone (Aldrich) was twice sublimed prior to use. Tributyltin hydride (TBTH) was prepared by reduction of tributyltin chloride. 2-Propanol-0-d (Merck) was used as received. 2-Propanol-O-d was prepared by exchange with D$_2$O.

Fluorescence and phosphorescence lifetimes were measured using the single photon counting technique. The air spark lamp used had a half-width of 1.8 nsec. Phosphorescence lifetimes were measured on degassed solutions in acetonitrile. Minor corrections were made for differences in absorbance at $\lambda_{ex}$ (310 nm).

Results and Discussion

We have studied solvent effects on the fluorescence lifetime, $\tau_f$, and relative fluorescence quantum yield, $\phi_{fl}$, for some adamantane derivatives (1).

states can fluoresce, and undergo intersystem crossing to the excited triplet state. The quantum yield of fluorescence ($\phi_f$) and the singlet lifetime ($\tau_s$) are then given by eq 4 and 5, respectively. As we can see from these equations, reaction of the adamantane $S_1$ state with the solvent (RH) would lead to a decrease in both $\phi_f$ and $\tau_s$, relative to a solvent in which no reaction occurs.

The data in Table I are perhaps best discussed in terms of the processes shown in Scheme I. The rate constants, $k_q$, calculated for quenching of the $n,\pi^*$ excited singlet state of 2-adamantanone by the various hydrogen donors (RH) are given in Table II.

The $k_q$ values for quenching by 2-propanol, tert-butyl alcohol, and TBTH were obtained from the slope of Stern–Volmer plots (eq 6) of $\tau_s^{-1}$ vs. [RH] in hexane as shown in Figure 1. For the alcohols, the Stern–Volmer plots, although they are clearly linear at high alcohol concentrations, definitely show some initial curvature (see Figure 1). This most likely indicates that we are seeing two "solvent effects" superimposed. One, which predominates at high alcohol concentrations, results in the linear portion of the Stern–Volmer plot with a slope of $k_q$. The extrapolated intercept of this linear portion of the $\tau_s^{-1}$ vs. [RH] plot should represent the "true" singlet lifetime for 2-adamantanone in alcohols in the absence of reaction with solvent.

Although rare, there are several documented cases of solvent effects of $k_f$ and $k_t$ could also be reflected in the changes in $\phi_f$ and $\tau_s$ values. A change in $k_f$ should lead to opposite effects on $\phi_f$ and $\tau_s$. For example, an increase in $k_f$ would make $\phi_f$ larger while decreasing $\tau_s$. It is clear from Table I, however, that decreases in $\tau_s$ are paralleled by decreases in $\phi_f$. Solvent effects on $k_q$ are possible, but it seems highly unlikely that they would lead to changes in $\tau_s$ values so systematically similar to what we would expect for hydrogen abstraction from the solvent (side infra).

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Similar intercepts of 0.116 nsec⁻¹ are obtained for both 2-propanol and tert-butyl alcohol, indicating a value of about 8.6 nsec for the “true” τp of 2-adamantane in alcoholic solvents. The kqt values for methanol and ethanol were obtained from the difference between the measured 2-adamantane τp value in these neat alcohols and this “true” τp value of 8.6 nsec for alcoholic solvents in the absence of bimolecular reaction.

Examining the rate constants in Table II we see that with the exception of tert-butyl alcohol, the kqt values increase as the strength of the weakest C–H bond in the donor decreases. Thus, for example, for the alcohols the reactivity increases in going from methanol (primary α-C–H) to ethanol (secondary α-C–H) to 2-propanol (tertiary α-C–H). This is precisely the type of structure-reactivity relationship that would be expected if the transition state for quenching involved partial cleavage of the weakest C–H bond in the quencher, i.e., for a hydrogen abstraction reaction. Further support for the involvement of the α hydrogens of the alcohol in the quenching is available from studies with deuterium-substituted 2-propanols. 2-Propanol–d3 is a considerably less efficient quencher than 2-propanol, whereas no significant difference is observed between 2-propanol–O–d and 2-propanol. For the potent hydrogen donor TBTH, the most reactive quencher, the possibility that part of the quenching effect that we are observing is heavy atom induced enhanced intersystem crossing is eliminated by the observation that tetrabutyltin does not quench τp of adamantane. The effect of quencher structure on the kqt values clearly can be reasonably rationalized by a quenching mechanism involving at least partial intermolecular hydrogen abstraction.

The apparent reactivity of tert-butyl alcohol as a singlet quencher is surprisingly high, if the quenching mechanism involves only intermolecular hydrogen abstraction. However, no single chemical or physical property of the alcohols studied would give rise to the order observed for singlet reactivity, i.e., i-PrOH > EtOH > t-BuOH > MeOH. Multiple effects are suggested by the curvature in the Stern–Volmer plots and perhaps yet another competing pathway, electron transfer, is involved in the complex quencher mechanism. This could account for the anomalously high reactivity of t-BuOH. The order of reactivity for electron transfer can be predicted from the ionization potential of the alcohol, i.e., t-BuOH > i-PrOH > EtOH > MeOH. Thus a combination of electron transfer and hydrogen abstraction could account for the complete order of reactivity obtained for singlet quenching.

As noted earlier there is considerable interest in the relative reactivity of alkanone excited singlet and triplet states toward intermolecular hydrogen abstraction. The rate constants for quenching by hydrogen donors of adamantane and various alkanes are given in Table II. The kqt values were obtained either from the literature or by measuring the quenching of the acetone phosphorescence lifetime (τp) at 25°C in acetonitrile as a function of added alcohol (eq 7).

Clearly there is a major discrepancy between the conclusions of our work and the earlier report that the S1 state of acetone is at least two to three orders of magnitude less reactive than the T1 state toward intermolecular hydrogen abstraction from TBTH. The latter conclusion was derived from the absence of photoreduction from S1 as demonstrated by the complete quenching of both 2-propanol formation and acetone disappearance in the presence of 5 M piperidine, which was assumed to be quenching only acetone T1 states. Although it is now known that piperidine quenches n,π* S1 as well as T1 states, singlet diene quenching is usually a relatively inefficient process. Even at the high concentrations of dienes used only partial, not complete, quenching of the S1 state would be expected. Another potential problem is the possibility of interaction of the hydroxy carbinyl radical (1), initially generated by hydrogen abstraction, with the diene quencher.

If a hydrogen transfer reaction such as shown in eq 8 were efficient it could lead at high diene concentration to total quenching of both formation of 2-propanol and disappearance of acetone, even if singlet intermolecular hydrogen abstraction were still occurring. Another intriguing possibility for explaining the apparent discrepancy between the earlier work and ours is that intermolecular hydrogen abstraction may be inherently much less efficient than the alkane S1 state than the alkane T1 state. Such an effect has been noted in the intramolecular hydrogen abstraction reactions of alkynes.


(22) Although Wagner observed no singlet photoreduction for acetone and 2-octanone, there have been several reports of singlet photoreduction of β,γ-unsaturated ketones. See E. Baggiolini, K. Schaffner, and O. Jeger, Chem. Commun., 1103 (1969); E. Baggiolini, H. P. Hamlow, and K. Schaffner, J. Amer. Chem. Soc., 92, 4906 (1970).

(23) The limits of detectability of acetone disappearance are unclear, as the experimental details have not been published.


nones, where although the reactivity of the $S_1$ and $T_1$ states are comparable, reaction via the $T_1$ state is much more efficient. A recent theoretical model of photochemical reactions in fact suggests that intermolecular hydrogen abstraction should be much less efficient from alkanone $S_1$ states than alkanone $T_1$ states. For the intermolecular case inefficiency could imply that abstraction is occurring (or partially occurring) but is rapidly followed by return of the hydrogen. Such a process would lead to fluorescence quenching without photoreduction from $S_1$, i.e., inefficient intermolecular hydrogen abstraction.

Thus while strong mechanistic evidence is admittedly difficult to obtain for photochemical reactions of low reactivity ($\sim 10^5 \text{ M}^{-1} \text{ sec}^{-1}$) arising from excited states of short lifetimes ($<10^{-6}$ sec), it is now clear that the possibility that singlet ketones are equally reactive as triplet ketones toward intermolecular hydrogen abstraction is a real one. If this is correct, then one of the major arguments for different mechanisms for intra-

...molecular $\gamma$-hydrogen abstraction from $S_1$ and $T_1$ states of alkanones is invalidated, further clearing the way for a unified theory of singlet-triplet reactivity in alkanone photochemistry. Another implication of our work is that when inefficient quenching ($k_{q} \leq 0.1$) of alkanones by hydrogen donors is observed, the quenching may be occurring from the alkanone singlet and/or triplet state. Thus the reported greater reactivity of triplet cyclopentanone than triplet cyclohexanone toward intermolecular hydrogen abstraction from 2-propanol may be subject to question. The triplet reactivities were derived from 2-propanol quenching of enal formation ($k_{q} \sim 0.04$ - 0.14). The inefficient quenching was assumed to represent only triplet quenching. If singlet quenching were also occurring the reported triplet reactivities would be incorrect.


### Nucleophilic Reactions of Sulfite Esters in Aqueous Media

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**Abstract:** The hydrolysis reactions of three sulfite esters, diphenyl sulfite (VIII), bis-p-nitrophenyl sulfite (IX), and phenyl p-nitrophenyl sulfite (X), in carboxylic acid buffers were examined as simple models for the corresponding pepsin-catalyzed processes. The observation of a substantial Bronsted $\beta$ value, 0.85, for the monocarboxylate ion catalyzed hydrolysis of VIII, as well as the finding that the kinetic solvent isotope effect ($k_{OH} / k_{DH}$) of VIII is 1.32, are consistent with the hypothesis that these reactions of VIII occur by nucleophilic catalysis. Similarly, the acetate-catalyzed solvolysis of IX and X is suggested to occur through a nucleophilic pathway. Support for the proposal that the nucleophilic attack of the carboxylate ions on the sulfites leads to the formation of mixed anhydride intermediates (eq 7) has been obtained by the detection of the acetohydroxamic acid produced when VIII, IX, and X are solvolyzed in acetate buffer in the presence of hydroxylamine. In the case of VIII measurement of the rate of acetohydroxamic acid production has indicated that under the conditions employed the rate-controlling step is mixed anhydride formation. In contrast to the solvolyses in carboxylic acid buffers, the direct kinetic detection of intermediates in the reactions of the sulfite esters VIII and X with hydroxylamine buffers has been accomplished. The rate constants for intermediate formation and decomposition were obtained by a computer-assisted kinetic analysis in the case of VIII and by observation of the reaction course at different wavelengths in the case of X. Through a combination of kinetic and synthetic experiments, the solvolysis of X in N,N-dimethylhydroxylamine buffer has been shown to proceed through the initial formation of phenyl methoxycarbonylaminosulfite (XI). The demonstration that reactive intermediates can be detected in model solvolytic reactions of sulfite esters provides encouragement for the search for conditions under which intermediates formed by nucleophilic attack by the active site enzymatic carboxylate groups of pepsin can be detected directly.

On the basis of kinetic studies and chemical modification data, the mechanism shown in Figure 1 involving the postulated formation of covalent enzyme-substrate intermediates has been proposed for the pepsin-catalyzed hydrolysis of sulfite esters. While direct evidence for the existence of intermediates like the anhydride species V during the course of these reactions is lacking, our observations on the inequality of the apparent Michaelis constant for the hydrolysis of diphenyl sulfite (VIII) and the inhibition constant for the inhibition of the hydrolysis of bis-p-nitrophenyl sulfite (IX) by added VIII besides those on the complexity of the $k_{cat}$ vs. pH profile for the hydrolysis of IX are strongly suggestive of the existence of such an intermediate.

In parallel with our investigation of the action of pepsin on sulfite esters, we have examined the catalytic effects of model carboxylic acids on the hydrolysis of sulfite esters. The objective of these studies has been to ascertain whether or not carboxylate ions act as

