

raise and lower the level of manometer fluid, a three-way stopcock, and a 25-ml vessel with a septum cap. The entire volume of the manometer was submersible. The temperature of the constant temperature bath used had to be maintained within $\pm 0.05^\circ$, since the reading sensitivity of the meniscus line of the manometer was $\pm 0.15 \mu\text{l}$.

Before immersing the apparatus in the bath, it was flushed with nitrogen for 30 min. During this time the manometer fluid was added and the stopcock opened to the nitrogen reservoir. The perester decomposition was used as the manometer fluid, in place of mercury, because of the increased sensitivity of less dense liquids to pressure change. Thermal equilibrium was attained only about 12 hr after immersion.

Since the perester solution was kept at a temperature 20–30° below that of the bath, in order to avoid decomposition, it was necessary to measure the effect of this temperature differential on the volume. Solvent aliquots at this lower temperature were syringed into the manometer, the stopcock was immediately closed, and the

volume change noted over the expected reaction period. If the volume changes of two consecutive solvent injections were within 5–10 μl of each other, then the perester stock solution was injected. After decomposition was complete, another blank was injected.

Esr Spectra and Uv-Vis Spectra of 1,1-Diphenylneopentyl Radical. Esr spectra were recorded on a Varian V-4502 X-band spectrometer using 100 kc modulation. A solution of Ic was syringed into an apparatus consisting of a quartz esr tube and a pyrex visible spectra sample tube sealed end to end with the aid of graded seals, with a T joint in the middle to a stopcock. The apparatus was flushed with nitrogen and the perester allowed to decompose. The esr spectrum of the resulting pale yellow solution was then recorded. The uv-visible spectrum was recorded on a Cary 14 instrument and found to consist of a tail into the violet region, without any maximum.

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Evidence for Comparable Reactivity of Alkanone Excited Singlet and Triplet States toward Hydrogen Donors¹

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Abstract: Studies of solvent effects on the relative fluorescence quantum yield ($\phi_{r^{e1}}$) and fluorescence lifetime (τ_s) of 2-adamantanone are presented. The ability of a given solvent to quench adamantanone 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 adamantanone excited singlet state. Kinetic studies indicate that the alkanone n, π^* singlet is just as reactive as the n, π^* triplet toward quenching by hydrogen donors.

The intermolecular photoreduction of alkyl ketones has been the subject of considerable interest over the past few years.^{5–10} 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.^{6–9} It has been reported that the alkanone n, π^* singlet state (S_1) is at least two or three orders of magnitude less reactive than the n, π^* triplet state (T_1) toward intermolecular hydrogen abstraction.^{6,8} 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.¹¹ 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, π^* singlet and n, π^* 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-*d*₈ (Merck) was used as received. 2-Propanol-*O-d* was prepared by exchange with D₂O.

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. Fluorescence yield measurements were carried out using a Hitachi-Perkin-Elmer MPF-2A spectrofluorometer. Minor corrections were made for differences in absorbance at λ_{ex} (310 nm).

Results and Discussion

We have studied solvent effects on the fluorescence lifetime, τ_s , and relative fluorescence quantum yield,

(11) See N. J. Turro, et al., *Accounts Chem. Res.*, 5, 92 (1972), and references therein.

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(5) P. J. Wagner, *J. Amer. Chem. Soc.*, 88, 5672 (1966).

(6) P. J. Wagner, *J. Amer. Chem. Soc.*, 89, 2503 (1967).

(7) R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 3751 (1967).

(8) P. J. Wagner, *Tetrahedron Lett.*, 5385 (1968).

(9) N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, 2, 39 (1970).

(10) For a recent review, see J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, 21, 499 (1970).

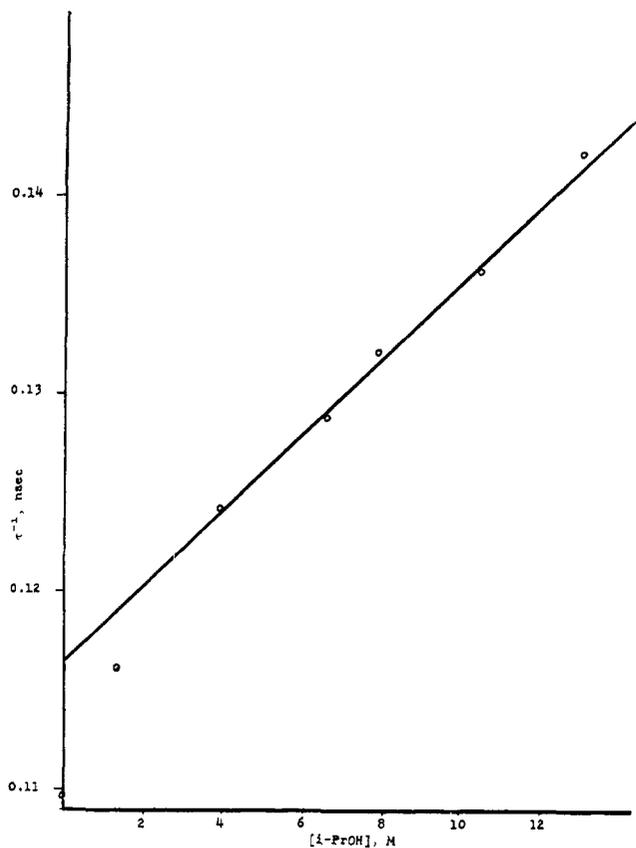


Figure 1. Isopropyl alcohol quenching of singlet lifetime of 2-adamantanone in hexane.

ϕ_f^{rel} , of 2-adamantanone, concentrating mainly on solvents which would be anticipated to have varying facility as hydrogen donors. The results are given in Table I. 2-Adamantanone was chosen because its rela-

Table I

Solvent ^a	$\phi_f^{\text{rel}b}$	τ_s , nsec ^c
Hexane	1.00	9.12
Methanol	0.91	8.10
Ethanol	0.87	7.41
2-Propanol	0.82	7.02
<i>tert</i> -Butyl alcohol	0.95	7.95

^a Solutions approximately 0.10 M 2-adamantanone in neat solvent. ^b Quantum yield of fluorescence measured relative to 2-adamantanone in hexane. ^c Fluorescence lifetimes measured by single photon counting technique. Absolute error $\pm 5\%$. Relative error $\pm 2\%$.

tively slow rate of decay by unimolecular pathways ($\tau_f = 9.1$ nsec in hexane) enables bimolecular processes to compete effectively. Although we report here only on 2-adamantanone, qualitatively similar behavior has been observed for several other alkanones.

The data in Table I are perhaps best discussed in terms of the processes shown in Scheme I. The initially generated 2-adamantanone excited singlet states (1A) can fluoresce (eq 1), undergo intersystem crossing to the excited triplet state (eq 2), or, in the presence of a reactive solvent, undergo an intermolecular reaction (eq 3). The quantum yield of fluorescence (ϕ_f) and the singlet lifetime (τ_s) are then given by eq 4 and 5, respectively. As we can see from these equa-

Scheme I



$$\phi_f = \frac{k_f}{k_f + k_{st} + k_q^s[RH]} \quad (4)$$

$$\tau_s = \frac{1}{k_f + k_{st} + k_q^s[RH]} \quad (5)$$

$$\tau_s^{-1} = k_f + k_{st} + k_q^s[RH] \quad (6)$$

$$\tau_T^{-1} = \tau_T^{-1} + k_q^t[RH] \quad (7)$$

tions, reaction of the adamantanone S_1 state with the solvent (RH) would lead to a decrease in both ϕ_f and τ_s , relative to a solvent in which no reaction occurs.¹²

The rate constants, k_q^s , calculated for quenching of the n, π^* excited singlet state of 2-adamantanone by the various hydrogen donors (RH) are given in Table II.

Table II

Hydrogen donor	$k_q^s, 10^6 M^{-1} \text{sec}^{-1} \text{ }^a$	$k_q^t, 10^6 M^{-1} \text{sec}^{-1} \text{ }^b$
Methanol	0.3	0.1, ^c 0.2 ^d
Ethanol	1.1	0.4 ^e
2-Propanol	1.9	1.0 ^d
<i>tert</i> -Butyl alcohol	0.9	0.004, ^f <0.005 ^d
TBTH	480	850 ^g

^a Rate constants for quenching of 2-adamantanone n, π^* singlet state. See text for methods of determination. ^b Rate constants for quenching of alkanone n, π^* triplet states by hydrogen donor. Unless specified otherwise alkanone was acetone. ^c Reference 20. ^d This work. See text for method of evaluation. ^e N. Schore, Columbia University, unpublished result. ^f Reference 21. ^g Reference 6.

The k_q^s values for quenching by 2-propanol, *tert*-butyl alcohol, and TBTH were obtained from the slope of Stern-Volmer plots (eq 6) of τ_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 and is fully manifested at low concentrations, is a genuine solvent effect on τ_s (probably k_{st}).¹³ The other "effect," which is a bimolecular reaction between adamantanone singlet state and the hydrogen donor, predominates at high alcohol concentrations, resulting in a linear portion of the Stern-Volmer plot with a slope of k_q^s . The extrapolated intercept of this linear portion of the τ_s^{-1} vs. [RH] plot should represent the "true" singlet lifetime for 2-adamantanone in alcohols in the absence of reaction with solvent.

(12) Solvent effects on k_f and k_{st} could also be reflected in the changes in ϕ_f and τ_s values. A change in k_f should lead to opposite effects on ϕ_f and τ_s . For example, an increase in k_f would make ϕ_f larger while decreasing τ_s . It is clear from Table I, however, that decreases in τ_s are paralleled by decreases in ϕ_f . Solvent effects on k_{st} are possible, but it seems highly unlikely that they would lead to changes in τ_s values so systematically similar to what we would expect for hydrogen abstraction from the solvent (*vide infra*).

(13) Although rare, there are several documented cases of solvent effects of k_{st} . So, for example, see R. A. Caldwell, *Tetrahedron Lett.*, 2121 (1969).

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" τ_s of 2-adamantanone in alcoholic solvents. The k_q^s values for methanol and ethanol were obtained from the difference between the measured 2-adamantanone τ_s value in these neat alcohols and this "true" τ_s value of 8.6 nsec for alcoholic solvents in the absence of bimolecular reaction.¹⁴

Examining the rate constants in Table II we see that with the exception of *tert*-butyl alcohol, the k_q^s 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.¹⁵ 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-*d*₈ 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 τ_s of adamantanone.¹⁶ The effect of quencher structure on the k_q^s values clearly can be reasonably rationalized by a quenching mechanism involving at least partial intermolecular hydrogen abstraction.¹⁷

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 singlet 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.¹⁸

As noted earlier there is considerable interest in the

(14) An experiment varying the methanol concentration was precluded by the lack of miscibility between hexane and methanol over a wide concentration range.

(15) See, for example, C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967); ref 6.

(16) G. Farrington, unpublished results.

(17) Irradiation of 2-adamantanone in hexane, methanol, ethanol, or 2-propanol results in formation of the photoreduction product, 2-adamantanol (J. J. Snyder, unpublished results).

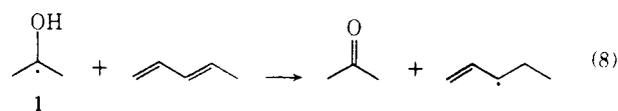
(18) Another possible quenching mechanism is the Heller mechanism¹⁹ which involves transfer of the electronic energy of the S_1 state to the CH bond, generating a highly vibrationally excited C-H bond. This mechanism has, however, recently been reported to be invalid for intermolecular hydrogen abstraction reactions of alkanone excited states.²⁰

(19) A. Heller, *Mol. Photochem.*, **1**, 257 (1969).

(20) R. W. Yip and W. Siebrand, *Chem. Phys. Lett.*, **13**, 209 (1972).

relative reactivity of alkanone excited singlet and triplet states toward intermolecular hydrogen abstraction. The rate constants for quenching by hydrogen donors of adamantanone n, π^* excited singlet states (k_q^s) and various alkanone n, π^* excited triplet states (k_q^t) are given in Table II. The k_q^t values were obtained either from the literature^{6-9, 20, 21} or by measuring the quenching of the acetone phosphorescence lifetime, τ_T , at 25° in acetonitrile as a function of added alcohol (eq 7). Clearly with the exception of *t*-butyl alcohol, the k_q^s value for quenching of 2-adamantanone S_1 states by a given hydrogen donor is comparable to the k_q^t value for quenching of alkanone T_1 states by the same donor over a reactivity range of nearly four orders of magnitude. Thus even allowing for some effects of ketone structure on reactivity, there certainly does *not* appear to be any significant difference in reactivity between S_1 and T_1 states of alkanones toward reaction with hydrogen donors.

Clearly there is a major discrepancy between the conclusions of our work and the earlier report that the S_1 state of acetone is at least two to three orders of magnitude less reactive than the T_1 state toward intermolecular hydrogen abstraction from TBTH.⁶ The latter conclusion was derived from the absence of photoreduction from S_1 ²² as demonstrated by the complete quenching of both 2-propanol formation and acetone disappearance in the presence of 5 M piperylene, which was assumed to be quenching only acetone T_1 states.²³ Although it is now known²⁴ that piperylene quenches n, π^* S_1 as well as T_1 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 S_1 state would be expected. Another potential problem is the possibility of interaction of the hydroxy carbonyl radical (1), initially generated by hydrogen abstraction, with the diene quencher.²⁵ 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 work⁶ and ours is that intermolecular hydrogen abstraction may be inherently much less efficient from the alkanone S_1 state than the alkanone T_1 state. Such an effect has been noted in the intramolecular hydrogen abstraction reactions of alka-

(21) G. Porter, R. W. Yip, J. W. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, 3149 (1971).

(22) Although Wagner observed no singlet photoreduction for acetone and 2-octanone,^{6,8} there have been several reports of singlet photoreduction of β, γ -unsaturated ketones. See E. Baggolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969); E. Baggolini, 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.

(24) (a) F. S. Wettack, G. C. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970); (b) N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971); (c) R. R. Hautala and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 5595 (1971).

(25) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Amer. Chem. Soc.*, **76**, 450 (1954).

nonenes, where although the reactivity of the S_1 and T_1 states are comparable, reaction *via* the T_1 state is much more efficient.¹⁰ 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.²⁶ 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 ($\sim 10^6 M^{-1} \text{sec}^{-1}$) arising from excited states of short lifetimes ($< 10^{-8}$ 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-

(26) J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972).

molecular γ -hydrogen abstraction from S_1 and T_1 states of alkanones²⁷ is invalidated, further clearing the way for a unified theory of singlet-triplet reactivity in alkanone photochemistry.²⁸

Another implication of our work is that when inefficient quenching ($k_q\tau \leq 0.1$) 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-propanol⁷ may be subject to question. The triplet reactivities were derived from 2-propanol quenching of enal formation ($k_q \sim 0.04$ – 0.14).⁷ The inefficient quenching was assumed to represent only triplet quenching. If singlet quenching were also occurring the reported triplet reactivities would be incorrect.

(27) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

(28) NOTE ADDED IN PROOF. For a recent study of quenching of acetone triplets by hydrogen donors see G. Porter, S. K. Dogra, R. O. Loutfy, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans. 1*, 1462 (1973).

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 Brønsted β value, 0.85, for the monocarboxylate ion catalyzed hydrolysis of VIII, as well as the finding that the kinetic solvent isotope effect $(k_{\text{OAc}}^{\text{H}_2\text{O}}/k_{\text{OAc}}^{\text{D}_2\text{O}} = 1.32$, 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,O*-dimethylhydroxylamine buffer has been shown to proceed through the initial formation of phenyl methoxymethylamidodisulfite (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.¹ 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

(1) S. W. May and E. T. Kaiser, *Biochemistry*, **11**, 592 (1972).

sulfite (IX) by added VIII² besides those on the complexity of the k_{cat} vs. pH profile for the hydrolysis of IX³ 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

(2) S. W. May and E. T. Kaiser, *J. Amer. Chem. Soc.*, **91**, 6491 (1969).

(3) S. W. May and E. T. Kaiser, *J. Amer. Chem. Soc.*, **93**, 5567 (1971).