Figure 1. Absorption spectra of 8×10^{-5} benzophenone in cyclohexane (a), in 2×10^{-3} M DODAC vesicles (b), and in 2×10^{-4} M DODAC vesicles incorporating 1.24×10^{-4} M Fe_3O_4 (c). The arrows indicate the directions of spectral change as functions of increasing amounts of absorbed 266-nm laser energies.

Figure 2. Laser flash photolysis of 8×10^{-5} M benzophenone in DODAC vesicles containing 0 (a), 0.205 (b), and 0.620 (c) molar ratios of Fe_2O_4. Excitation by 266-nm 8-ns pulses, observation at 545 nm. A_e and A_0 values indicated in the figure were obtained by computer extrapolations. Insert: Plots of percent of the escaped radicals as functions of the molar ratio Fe_3O_4 to DODAC (according to eq 1).

matrices of surfactant vesicles. Single-domain magnetic particles have effectively split the triplet sublevels of the radical pair localized in close proximity and slowed down its intersystem crossing from the T_+ and T_- sublevels.[2-6] This, in turn, enhanced the efficiency of radical escape which has manifested in decreased LAT production (Scheme I). Thus, the observed effect of the photochemistry of benzophenone is a direct result of the magnetic moment in the vicinity of the magnetic particles. We are not unaware of the significance of finding magnetic effects in the absence of magnets and are currently exploring the potential applications of this phenomenon.

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triplets, $^3BP^*$, and the subsequently formed ketyl radicals both absorb at 545 nm. Addition of 10^{-3} M 1,4-cyclohexadiene (RH in Scheme I) efficiently quenched $^3BP^*$, which resulted in the clear separation of two consecutive decays: a fast one, due to the decay of $^3BP^*$ and intersystem crossing, and a slower one, due to $\dot{K}H$ (Figure 2). The ratio of absorbance obtained by extrapolating the longer lived component to zero time, A_e, to the absorbance observed immediately after the laser flash, A_0[7a,b] is a measure of the importance of the escape process:

$$\frac{A_e}{A_0} = \frac{\Sigma k_-}{\Sigma k_- + k_{ISC}} \quad (1)$$

As seen in the insert of Figure 2, introducing increasing amounts of magnetite per DODAC vesicle resulted in increased amounts of escaped $\dot{K}H$. The effect obtained with 0.6 molar ratio of Fe_3O_4/DODAC ($87.6 \pm 3\%$) corresponds, within the limits of experimental error, to the maximum effect attainable.[17] The magnitude of the magnetic effects in the absence of magnets is the same as that found by applying an external field of approximately 2000 G.[7] In fact, an increase of exit from 55% to 84% was observed in dodecyltrimethylammonium chloride when a 2000-G magnetic field was applied.[7]

The determined binding contant, $K = 2 \times 10^4$ M^{-1}, indicated the complete incorporation of benzophenone into the magnetite carrying DODAC vesicles. Magnetic effects reported here originate, therefore, in the localization of benzophenone within the influence of single-domain magnetic particles confined in the
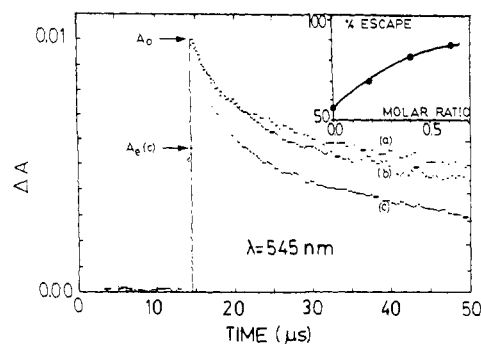
(16) Using the fourth harmonic of a Quanta-Ray DCR-1A Nd:YAG laser as the excitation source.[13]

(17) $85 = 55 + \frac{2}{3} (100 - 55)$.[7]

Concerning the Lifetime of the Second Excited Singlet State of Adamantanethione

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Thiones are prominent among the growing group of organic molecules known to react chemically and/or fluoresce from excited singlet states higher than S_1.[2,3] Of the various aromatic, aralkyl, and alicyclic thiones which are members of this group, only two, thiobenzophenone and adamantanethione, have been the subject of extensive investigations of their S_2 photochemistry.

Excitation in the first strong absorption band of adamantanethione (1) near 250 nm populates the second excited singlet state, of $^1(\pi,\pi^*)$ character.[4] The end products of illuminating 1 at 254 nm in cyclohexane solution arise from the net insertion of the thione into C–H bonds of the solvent and from dimerization. There is good evidence that a free radical mechanism is operative.[5,6] Kinetic arguments, based on concentration quenching and quenching by 1,1'-azoisobutane, have been used to determine that the reactive precursor to both insertion and dimerization products has a lifetime of ca. 250 ps.[5-7] It has always been assumed in the aforementioned work that the reactive precursor is the second

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(7) An earlier estimate[4] of ca. 130 ps was revised.

excited singlet state of **1**. However, recent experiments have led us to conclude that, although the reactive species produced when **1** is illuminated in its $S_2 \leftarrow S_0$ absorption band in cyclohexane may indeed have a lifetime of ca. 250 ps, that species is not the second excited singlet state of adamantanethione.

1 was prepared by the method of Greidanus[8] and was purified by low-temperature crystallization from *n*-pentane followed by HPLC. Adamantanone (**2**), a common impurity readily identified by its fluorescence, could only be removed by excluding oxygen at every stage of the purification of **1**. A pure sample of **2** was obtained by repeated sublimation of a commercial product (Aldrich). Pentane (BDH, LC grade) and perfluoro-*n*-hexane (PCR, redistilled) were free from measurable fluorescence when excited in the $\lambda_{ex} > 230$ nm range. Fluorescence spectra and quantum yields were obtained on a Spex, Model 222, Fluorolog instrument, which employs single photon counting detection and digital spectral correction. Fluorescence quantum yields were measured relative to quinine bisulfate in 1.0 N H_2SO_4 ($\phi_f = 0.54$).[9] Fluorescence lifetimes were measured with a frequency-doubled, cavity-dumped, synchronously pumped dye laser system described previously.[10]

No measurable emission in the 300 nm $< \lambda_{em} < 550$ nm range could be observed when degassed pentane or perfluoro-*n*-hexane solutions of **1** at room temperature were illuminated in the $S_2 \leftarrow S_0$ absorption band. The quantum yield of adamantanethione's $S_2 \rightarrow S_0$ fluorescence, ϕ_f, must therefore be less than 5×10^{-5} on the basis of the known sensitivity of the emission spectrometers. By contrast, both dilute pentane and perfluoro-*n*-hexane solutions of **2**, illuminated in its $S_1 \leftarrow S_0$ (n $\rightarrow \pi^*$) absorption band at $\lambda_{ex} = 290$ nm, gave readily measurable emission with $\phi_f = 6 \times 10^{-3}$, in moderate agreement with a previous value of ca. 15×10^{-3} in acetonitrile.[11] The fluorescence lifetime of **2** (2×10^{-3} M in pentane), excited at 297 nm, was 9.1 ± 0.1 ns, in excellent agreement with a previous report of 9.12 ns in hexane.[12]

Adamantanethione is a rigid molecule and its $S_2 \leftarrow S_0$ radiative transitions are electric dipole allowed. It should therefore be possible to estimate accurately the intrinsic radiative lifetime of the S_2 state of **1**, $\tau_{S_2}^0$, by the integrated absorption method of Strickler and Berg.[13] There is some uncertainty in this estimate because of the difficulty in separating the $S_2 \leftarrow S_0$ absorption from an overlapping, higher energy (likely Rydberg) transition of lower intensity with λ_{max} near 223 nm. Nevertheless, a reasonably secure value of $\tau_{S_2}^0 = 1.6 \times 10^{-9}$ is (leading to $k_r = 1/\tau_{S_2}^0 = 6.3 \times 10^8$ s^{-1}) can be obtained. The difference between this calculated should be no more than a factor of 2, considering the success achieved in calculating $\tau_{S_2}^0$ for the S_2 states of several rigid, fluorescent aromatic thiones by the same method.[14,15] The actual lifetime of the second excited singlet state of **1** is given by $\tau_{S_2} = \tau_{S_2}^0 \phi_f$. Since $\phi_f < 5 \times 10^{-5}$, τ_{S_2} should be less than ca. 10^{-13} s. Even if errors in estimating the lower limit of ϕ_f and in calculating $\tau_{S_2}^0$ are much larger than anticipated, the S_2 lifetime of **1** must still be considerably less than a picosecond. Such an estimate of τ_{S_2} is consonant with the complete absence of vibronic structure in the $S_2 \leftarrow S_0$ absorption system of **1** in any solvent. Thus, the reactive species observed by de Mayo and co-workers[4-6] having a lifetime of ca. 250 ps cannot be the second excited singlet state of **1**.

There are several possible alternate identities for the 250-ps intermediate. The broad, unstructured nature of the $S_2 \leftarrow S_0$ absorption band suggests that S_2 may undergo a prompt intra-

molecular reaction. However, neither of the most likely photoprocesses, excited-state isomerization to form either strained enethiol or cyclopropanethiol and α C–C bond cleavage to form a biradical, would likely lead to the final products that are observed when **1** is illuminated in alkane solution and in the presence of olefins.[4] The involvement of a higher triplet can be excluded on the basis of sensitization experiments.[4] By this process of elimination, reactive intermediates derived from intermolecular interactions between S_2 and the cycloalkane solvent must be considered.

We have shown recently[16,17] that alkanes (and many other addends) quench the second excited singlet states of several aromatic thiones at diffusion-controlled rates. The branching ratio between "physical" and net "chemical" quenching paths is of the order of 100:1 for 2,2,3,3-tetramethylindanethione in alkane solvents.[17] The second excited singlet state of **1** is likely much more chemically reactive than that of any aromatic thione because its excitation energy is considerably higher and its orbitally unpaired electrons are highly localized on the C–S moiety. Thus, highly indiscriminate H abstraction (as observed[5,6]) by the excited thione within the solvent cage on a subpicosecond time scale is entirely reasonable. Alternatively, a dark exciplex of 250-ps duration could be formed from S_2–solvent interaction. Such an exciplex might be expected to radiationlessly decay, in part, to adamantanethione S_1, which is known to intersystem cross quantitatively to the phosphorescent T_1 state;[18] weak phosphorescence is observed in our experiments when **1** is illuminated in its $S_2 \leftarrow S_0$ absorption band in both alkane and perfluoroalkane solutions. Picosecond transient absorption spectroscopy should prove to be very useful in identifying the reactive transient unambiguously.

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Novel Oxidative Dehydrogenation Reaction of α-Amino Acids Chelated to Cobalt(III) Ion: Synthesis of (2-Iminocarboxylato)cobalt(III) Complexes

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Coordinated amine compounds such as diamines or macrocyclic tetraamines are known to be dehydrogenated to imine compounds.[1] The oxidative dehydrogenation of 1,2-diamines of Fe(II),[2] Ru(II),[3] Os(II),[4] and Pt(IV)[5] complexes by chemical and/or electro-

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