Fluorescence from Samarium(II) Iodide and Its Electron Transfer Quenching: Dynamics of the Reaction of Benzyl Radicals with Sm(II)

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The luminescence from SmI_2 in THF can be readily quenched by a variety of electron acceptors. In the case of organohalides, the reaction is quite fast; for example, for dichloromethane the rate constant is 2.7×10^8 M^{-1} s^{-1}. Electron transfer leads to halide loss and formation of the carbon-centered radical. In the case of benzyl chloride, the benzyl radicals produced can be readily detected using laser flash photolysis techniques. This electron-transfer reaction has been used as a source of benzyl radicals in order to determine the rate constant for their reaction with SmI_2; the value obtained is $(5.3 \pm 1.4) \times 10^7$ M^{-1} s^{-1} in THF at room temperature. The effect of HMPA on the spectroscopic properties of SmI_2 has also been examined.

Introduction

Samarium iodide (SmI_2) is widely employed as a reducing agent in organic chemistry.[1−11] The reactions are believed to be mediated by free radicals and are occasionally initiated photochemically, although the photochemical properties of SmI_2 have not been examined in any detail. SmI_2 in THF is known to be fluorescent,[12−14] but to the best of our knowledge, its lifetime and quenching characteristics have not been reported. The emission is believed to involve the transition from the $4f^5$ 5d to the $4f^6$ state.[13−16]

One key step in any mechanism involving the reduction of organic substrates by SmI_2 is the reaction of free radicals with Sm(II). In the case of primary alkyl radicals, Hasegawa and Curran have estimated a rate constant of 7×10^6 M^{-1} s^{-1} in the presence of an excess of HMPA (hexamethylphosphoramide).[17] We initiated our work in this area in the hope of determining an absolute rate constant for the reaction of carbon-centered free radicals, in particular $C_6H_5CH_2^{\bullet}$ (which is readily detectable) with Sm(II). Our original goal was to determine this value by generating benzyl radicals from photodecomposition of dibenzyl ketone in the presence of various concentrations of SmI_2. Unfortunately, it was impossible with our equipment to find a wavelength where we could photodecompose dibenzyl ketone without predominantly irradiating SmI_2. As our experiments progressed and we attempted to understand better the photochemistry of Sm(II), we realized that the electron-transfer reactions of SmI_2 provided an alternate clean way of generating benzyl radicals from the corresponding benzyl halides.

In the work reported here we have performed a time-resolved study of the excited states of Sm(II). For these measurements, we have utilized nanosecond laser photolysis techniques combined with time-resolved emission spectroscopy and transient absorption detection. Excited Sm(II) is an excellent electron donor,[12] and we have studied its reactivity toward a variety of substrates, predominantly electron acceptors. The reactions with benzyl halides provide access to a viable source of benzyl radicals, thus allowing the determination of the absolute rate constant for their reaction with Sm(II), and, in the process, to an understanding of some aspects of the photochemistry and photophysics of SmI_2.

Experimental Section

Samarium(II) iodide was purchased from Aldrich as a 0.1 M solution in tetrahydrofuran (THF) and used as received. The standard solvent for this work was THF (from Aldrich), which was dried by distillation over sodium−potassium alloy under nitrogen and used immediately. While SmI_2 can be usually handled with simple "sure-seal" techniques at the concentrations used for synthetic work, spectroscopic work with millimolar concentrations of Sm(II) requires drybox handling under oxygen-free and water-free conditions. Hexamethylphosphoramide (HMPA) and dibenzyl ketone (from Aldrich) were used as received. The electron acceptors used as quenchers for Sm(II) fluorescence were obtained from Aldrich and used as received except for drying them with $MgSO_4$, $CaCl_2$, P_2O_5, or activated alumina.

In our work, we have employed steady-state and time-resolved techniques to study the luminescence from SmI_2 in THF. Steady-state experiments were performed with a Perkin-Elmer LS-50 spectrofluorimeter. Time-resolved luminescence work used attenuated 355 or 532 nm pulses from the harmonics of a Surelite Nd/YAG nanosecond laser for excitation (≤20 mJ per 6 ns pulse). The emission was monitored with a system consisting of a spectrograph and a Hamamatsu C-4334 Streakscope, capable of simultaneous spectral and time-resolved data acquisition with nano- or picosecond resolution. All experiments were carried out at room temperature

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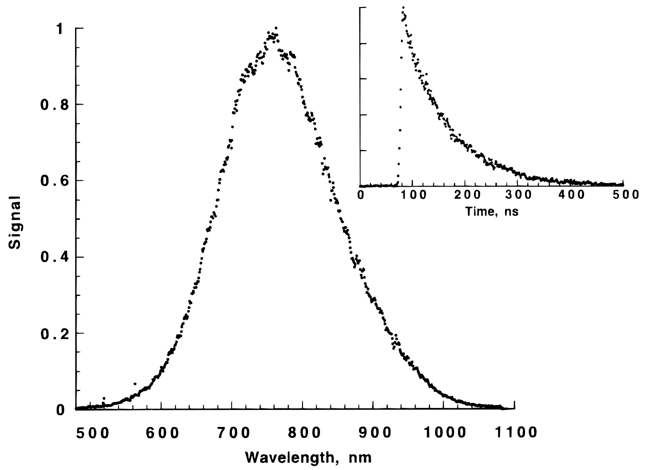

Figure 1. Luminescence spectrum from SmI_2 in THF following 355 nm excitation and fluorescence decay (inset) monitored in the 730−770 wavelength window using a streak camera for detection.

in nitrogen-saturated samples contained in either 7 × 7 mm or 10 × 10 mm quartz cells.

Laser photolysis experiments were carried out using for excitation either the same laser as above or an excimer laser operated at 308 nm. The rest of the excitation and detection system were similar to those described earlier.[18]

Results

All of our work was carried out at room temperature, and THF was the solvent of choice. The sections below are divided according to the type of measurement involved.

Emission Spectroscopy. Figure 1 illustrates the emission spectrum recorded following 355 nm laser excitation of SmI_2; it shows λ_{max} ~760 nm and (see inset) a decay lifetime of 83 ns. The lifetime of this emission showed significant variations on a day-to-day basis; values between 61 and 110 ns have been recorded for an 8.5 mM solution (average 82 ns, $\sigma = 14$ ns). A study of the concentration dependence of this lifetime (4−20 mM range) revealed shorter lifetimes at the higher SmI_2 concentrations. This may be due to self-quenching by SmI_2 or, more likely, to quenching by impurities present in the commercial solutions of SmI_2 in THF or introduced during handling.[19] The lifetime extrapolated to zero SmI_2 concentration was ~125 ns and should correspond to the *true* value for SmI_2 in THF. Extrapolation to zero concentration should also eliminate any concerns relating to possible SmI_2 aggregation.

The rate constants for fluorescence quenching by various electron acceptors can be determined from the slope of plots of the reciprocal emission lifetime (τ^{-1}) as a function of quencher concentration (eq 1), as illustrated in Figure 2 for dichloromethane and chloroform.

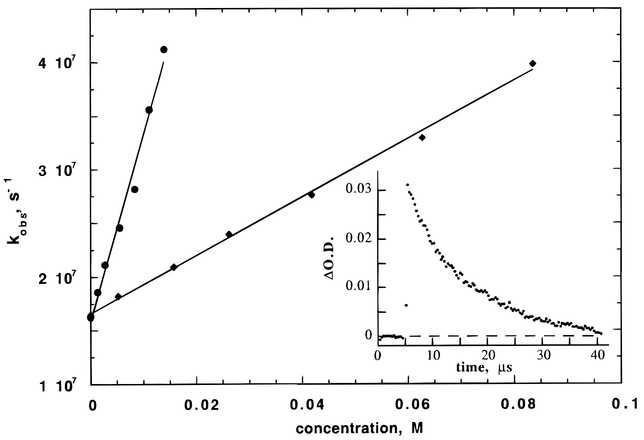

Figure 2. Fluorescence quenching plots for dichloromethane (♦) and chloroform (●). Inset: Decay of the benzyl radical monitored at 318 nm (transient absorption) following 308 nm excitation of a sample containing 3.2 mM SmI_2 and 29 mM benzyl chloride.

Table 1. Rate Constants for the Quenching of SmI_2 Luminescence by Electron Acceptors in THF at Room Temperature

substrate	k_q (M^{-1} s^{-1})[a]	substrate	k_q (M^{-1} s^{-1})[a]
CCl_4	2.7×10^{10}	$C_6H_5CH_2Cl$	5.9×10^8
$CHCl_3$	1.8×10^9	$C_6H_5CCl_3$	2.9×10^{10}
CH_2Cl_2	2.7×10^8	C_6H_5F	~8×10^6
$CH_3CHClCH_3$	6.9×10^7	C_6H_5Br	2.8×10^8
$(CH_3)_3CCl$	4.1×10^7	$C_6H_5CO_2CH_3$	4.1×10^9
CH_2ClCH_2Cl	1.1×10^8	$C_6H_5CO_2CH_2CH_3$	3.8×10^9

[a] Errors ± 5%.

$$\tau^{-1} = \tau_o^{-1} + k_q[\text{quencher}] \qquad (1)$$

The slopes of these plots correspond to the bimolecular rate constants for excited state reaction with the quencher. Studies of this type with several substrates led to the rate constants in Table 1. Errors in the lifetimes (*vide supra*) should have no effect on the determination of bimolecular rate constants. Steady-state quenching studies led to Stern−Volmer slopes ($k_q\tau$) in reasonable agreement with the independent values of k_q and τ determined in the time-resolved work. For example, for chloroform the Stern−Volmer slope was 124 M^{-1}, compared with a value of 107 M^{-1} calculated from the time-resolved experiments.[20] The corresponding values for ethyl benzoate are 567 (Stern−Volmer) and 328 M^{-1} (time resolved). For the halogenated compounds, electron transfer is followed by dissociation with loss of a halide ion. In those cases where the resulting radical has observable absorptions in the UV−vis region this was unequivocally established by direct detection of this radical. For example, this was the case for benzyl halides leading to the detection of $PhCH_2^{\bullet}$. The sequence of reactions for the case of benzyl chloride is shown in eq 2.

$$C_6H_5CH_2Cl \xrightarrow[k_{et}]{SmI_2^*} [C_6H_5CH_2Cl]^{\bullet-} \xrightarrow{\text{fast}} C_6H_5CH_2^{\bullet} + Cl^- \qquad (2)$$

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[18] The laser system uses Lumonics EX-510 and EX-530 for excitation wavelengths of 248 and 308 nm, Surelite lasers from Continuum for the Nd-YAG wavelengths of 266, 355, and 532 nm, and a Molectron UV-24 nitrogen laser for 337 nm. All pulse durations are <10 ns and typical pulse energies between 5 and 50 mJ. The signals from the monochromator/photomultiplier system were initially captured by a Tektronix 2440 digitiger and transferred to a PowerMacintosh computer that controlled the experiment with software developed in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of the system are similar to those described earlier: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

[19] This question cannot be resolved at this time because the concentration of such potential impurities will be proportional to the SmI_2 concentration. There are considerable experimental difficulties in handling very dilute solutions of air- and water-sensitive substrates; this may have contributed to the dispersion in the experimental emission lifetimes.

[20] Based on a lifetime of 61 ns determined for that particular experiment. See above for a discussion of the reproducibility of these lifetimes.

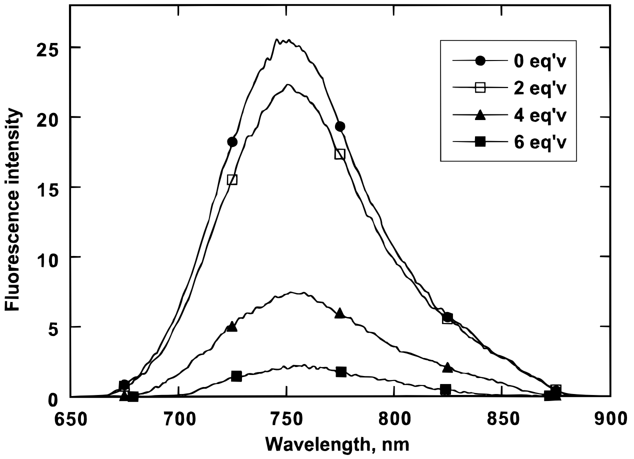

Figure 3. Effect of HMPA addition on the emission intensity from SmI_2 in THF.

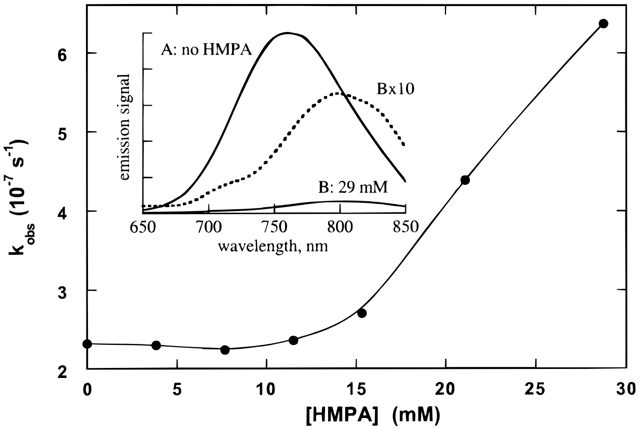

Figure 4. Effect of HMPA concentration on the fluorescence lifetime of Sm(II) in THF for emission data in the 700−860 nm window, for $[SmI_2] = 6$ mM ($\tau^{-1} = k_{obs}$). Inset: Spectra collected during the first 100 ns following laser excitation, based on the same time-resolved data as the main part of the figure.

Steady-state fluorescence experiments showed that the emission intensity from SmI_2 was greatly reduced upon addition of HMPA (Figure 3), a reagent frequently used in organic chemistry[2,5,8,17] to increase the reducing ability of SmI_2. Parallel time-resolved experiments showed that for HMPA/SmI_2 stoichiometric ratios ≤ 2, the fluorescence lifetime did not change at all in spite of the extensive quenching observed in steady state experiments (compare Figures 3 and 4). The steady state and time-resolved results can be rationalized by assuming that HMPA addition removes from the system the highly fluorescent SmI_2−$(THF)_n$ complex; further, HMPA coordination leads to a new complex with a much lower quantum yield for emission. The emission from SmI_2−$(THF)_n$ tends to dominate, and only when more than 2 equiv of HMPA are present can one detect a reduction in the lifetime. A red shift in the fluorescence spectrum to ~820 nm becomes evident only at very high HMPA concentrations and is best detected in the time-resolved measurements (see inset in Figure 4); this emission is presumed to be due to the HMPA complex. For example, for [HMPA] = 29 mM and $[SmI_2] = 6$ mM, the lifetime is only 16 ns.

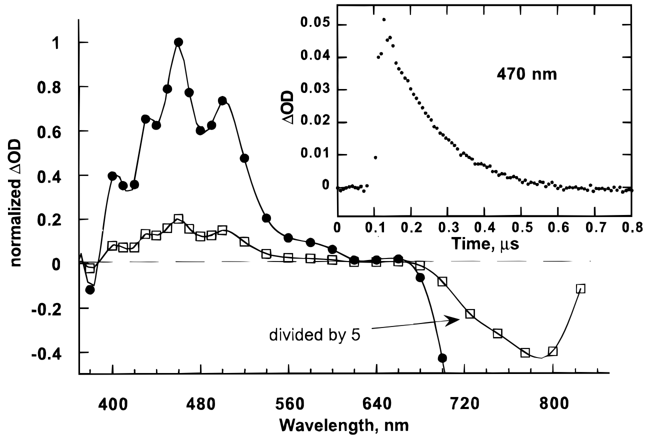

Figure 5. Normalized transient absorption spectra recorded following 308 nm laser excitation of 6 mM SmI_2 in THF (●). The open squares have been divided by five and show an inverted signal around 780 nm; this signal is due to the fluorescence from the complex. The inset shows a transient absorption decay trace (under the same conditions) monitored at 470 nm.

Laser Flash Photolysis Detection of Excited Samarium Intermediates. A series of experiments was also performed in order to characterize the excited state of Sm(II) by using laser flash photolysis techniques. In those regions where SmI_2 absorbs strongly, the signals are dominated by the bleaching and recovery of the ground-state absorption. In addition, excited Sm(II) shows significant absorptions in the 470 nm region (Figure 5). The inset in Figure 5 shows a transient absorption decay trace monitored at 470 nm; the lifetime derived from this trace was 125 ns. This lifetime is in excellent agreement with those obtained by extrapolation to zero concentration in the case of fluorescence measurements (*vide supra*). In fact, we were rather surprised with the ease with which these relatively long lifetimes could be obtained in the laser flash photolysis experiments. In hindsight, it seems likely that in this case the higher laser doses required lead to the sacrificial depletion of trace concentrations of impurities (such as oxygen and water) that may tend to survive longer (and thus influence the lifetimes) under the lower dose conditions of fluorescence measurements.

In the absence of electron acceptors the samples were remarkably resistant to prolonged laser excitation. For example, the spectrum of Figure 5 required over 200 laser shots, yet, it could be obtained with a static sample (with periodic stirring).

Laser Flash Photolysis Study of the Benzyl Radical−Sm(II) Reaction. All of our attempts to study the reaction of benzyl radicals from dibenzyl ketone with Sm(II) were frustrated by the extensive spectral overlap between the ketone and SmI_2 that prevents the selective excitation of the ketone precursor. Fortunately, the electron-transfer reactions of excited SmI_2 described earlier provide a clear alternate route for the generation of benzyl radicals in the presence of Sm(II). Thus, benzyl radicals could be generated through the electron-transfer quenching of excited SmI_2 as shown in reaction 2. The experiment was nonetheless rather difficult because the modest reaction rate constant (*vide infra*) forces the use of SmI_2 in concentrations high enough to lead to higher absorptions at the laser wavelength than values usually preferred for laser photolysis work. To some extent, this can be compensated by using laser cells of variable optical path, but shock wave generation can become unavoidable at high concentrations. The detection of benzyl radicals with their characteristic absorption around 317 nm[21]

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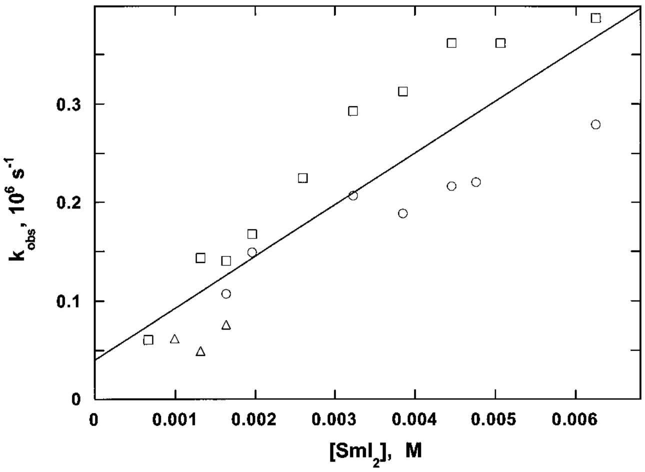

Figure 6. Scavenging of benzyl radicals generated according to reaction 2 by Sm(II). The data were monitored at 318 nm, following 308 nm laser excitation of THF solutions containing 29 mM benzyl chloride. The different shapes of points correspond to data obtained on different days.

confirmed the mechanism of the quenching process. Our experiments cannot distinguish between concerted and stepwise radical elimination,[22,23] although in the case of benzyl chloride we favor the latter, as shown in reaction 2.

The decay of benzyl radicals followed first-order kinetics in all of our experiments, suggesting that radical recombination does not play an important role under our experimental conditions. The determination of the rate constants for radical decay in the presence of variable concentrations of SmI_2 proved very difficult. The rate of electron transfer, k_{et}, is related to the rate constant for radical decay, i.e., the reciprocal of the radical lifetime, according to eq 3.

$$k_{decay} = k_o + k_{et}[Sm(II)] \qquad (3)$$

Figure 6 shows a plot according to eq 3, from which we derive a rate constant of $(5.3 \pm 1.4) \times 10^7$ M^{-1} s^{-1}. The data in Figure 6 were derived from experiments performed on three consecutive days and each point is in most cases the average of two or three independent determinations on the same day. Note how the results from different days tend to show systematic differences; we have found that these experiments are only reproducible within the limits shown in Figure 6. Any impurities, even water contamination, tend to lead to *systematic* errors that lead to good linear plots in spite of the errors. We believe the rate constant derived here is the best that can be achieved with current techniques, given the low concentrations required for this work, and the high sensitivity of Sm(II) to trace impurities. Our value is slightly higher than that determined by Hasegawa and Curran, who estimated a rate constant of 7×10^6 M^{-1} s^{-1} for primary radicals. However, this reported value was obtained in the presence of HMPA, which as already indicated has a strong effect on excited Sm(II) behavior.[17]

Discussion

Excited SmI_2 is strongly fluorescent in THF, where its lifetime is ~125 ns (at $c \rightarrow 0$). Addition of HMPA, a reagent frequently employed in organic reductions with Sm(II), causes a dramatic reduction in the emission intensity (Figure 3). Interestingly, when less than 2 equiv of HMPA is used this quenching of the emission intensity is not accompanied by any detectable change in the emission lifetime (compare Figures 3 and 4). We believe that in contrast to the high fluorescence yield for the $SmI_2-(THF)_n$ complex, species containing one or more HMPA ligands have very weak fluorescent properties. Thus, as long as some $SmI_2-(THF)_n$ complex remains present, the emission is dominated by this species. Only at high HMPA$-SmI_2$ ratios one can detect a shortening of the lifetime, Figure 4. Interestingly, the decays at high HMPA still follow first-order kinetics, suggesting that excited Sm(II) species with one or more HMPA ligands equilibrate rapidly. The red shift in the emission is only detectable (λ_{max} 820 nm) when 6 equiv of HMPA are present, compared with ~760 nm in the absence of HMPA. Regardless of any redox considerations, it is clear that in photoinduced electron-transfer processes the $SmI_2-(THF)_n$ complex will be more efficient (even if this complex is not necessarily more reactive) than Sm(II)$-$HMPA species, reflecting that the short excited-state lifetime of the latter will make it difficult to quench.

The rate constants for electron transfer to halogenated acceptors follow the order of their known electron acceptor abilities; thus, for CH_2Cl_2, $CHCl_3$, and CCl_4 the relative reactivities are 1:6.4:100. A similar trend is observed with benzylic acceptors. Electron transfer is followed by fragmentation to yield the halide anion and the corresponding radical. In resonance-stabilized systems (e.g., benzyl), the radicals are readily detectable in laser flash photolysis experiments.

The rate constant for the reaction of benzyl radicals with Sm(II) has been determined as $(5.3 \pm 1.4) \times 10^7$ M^{-1} s^{-1} in THF. The value is comparable with that reported for primary radicals in the presence of HMPA,[17] although it should be noted that the rate constants are expected to be strongly influenced by HMPA. The determination was based on the generation of benzyl radicals by electron transfer from excited SmI_2, since alternate sources of these radicals (e.g., dibenzyl ketone) are impractical due to extensive spectral overlap between these precursors and samarium iodide.

Conclusion

In summary, the highly fluorescent excited state of SmI_2 in THF has a lifetime of ~125 ns and is readily quenched by a variety of electron acceptors. The same intermediate can also be detected in laser photolysis experiments and has a characteristic absorption centered around 470 nm. Organic chlorides lead to the formation of chloride ion and free radicals from the dissociative or short-lived radical anion, confirming that at least photoinitiated SmI_2 reactions are mediated by free radicals. HMPA addition changes the fluorescent properties of Sm(II), and these changes show a threshold at a 2:1 stoichiometric ratio (HMPA:SmI_2). Benzyl radicals react with Sm(II) with a rate constant of $(5.3 \pm 1.4) \times 10^7$ M^{-1} s^{-1} in THF.

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