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Detection of Transient Intermediates in the Photochemical Reaction of Hydrogen Peroxide with Dimethyl sulfoxide by Time-Resolved EPR Techniques

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In the photochemical reaction of hydrogen peroxide with dimethyl sulfoxide, three spin-polarized transient radical species have been identified by time-resolved EPR techniques: $(CH_3)_2SO(OH)^\bullet$ (I), ${}^\bullet CH_3$ (II), and ${}^\bullet CH_2SOCH_3$ (III). The assignments are based on the observed spectral parameters, the deuteration effect, and the time profile analyses. However, the identification of adduct radical (I) is somewhat tentative. To explain the nonrelaxation-limited polarization observed in ${}^\bullet CH_3$ radicals, a cyclic pathway to continuously regenerate ${}^\bullet CH_3$ is proposed and verified experimentally. The time evolution of the polarized spin adducts further allows one to follow the entire course of the reaction pathway, yielding important details on the reaction mechanism.

Introduction

It has been reported that dimethyl sulfoxide (DMSO) is a potent hydroxyl radical scavenging agent (${}^\bullet OH$). The antiinflammatory activity of DMSO has been ascribed to the ability of this compound to scavenge ${}^\bullet OH$ and peroxy radicals.[1] The reaction of ${}^\bullet OH$ radicals with DMSO can yield methyl radical (${}^\bullet CH_3$) intermediates which can further produce methane and ethane (through dimerization of methyl radicals) as the final products.[2] The methyl radicals may also react with molecular oxygen to form peroxy radicals ($CH_3OO^\bullet$), which can result in the formation of formaldehyde via a Russell-type mechanism.[1] Thus, the production of methane, ethane, and formaldehyde in the presence of DMSO has been utilized as a marker to quantify ${}^\bullet OH$ radical-induced oxidation in biological systems. [1−3]

It has been reported that ${}^\bullet OH$ radicals can abstract an α hydrogen from alcohol and acetate,[4] or they can directly add to a reactant.[2] The following mechanisms have been proposed to explain the observed product formation from the photochemical reaction of hydrogen peroxide with DMSO.

$$H_2O_2 \xrightarrow{h\nu} 2OH^\bullet \tag{1}$$

$$(CH_3)_2SO + {}^\bullet OH \rightarrow \underset{(I)}{(CH_3)_2SO(OH)^\bullet} \rightarrow \underset{(II)}{{}^\bullet CH_3} + CH_3SO_2H \tag{2}$$

$$(CH_3)_2SO + {}^\bullet OH \rightarrow \underset{(III)}{{}^\bullet CH_2SOCH_3} + H_2O \tag{3}$$

$$(CH_3)_2SO + {}^\bullet CH_3 \rightarrow \underset{(III)}{{}^\bullet CH_2SOCH_3} + CH_4 \tag{4}$$

The rate of reaction of ${}^\bullet OH$ radical with sulfoxide is practically diffusion controlled; for example, a bimolecular rate constant of $k = 7 \times 10^9$ L mol^{-1} s^{-1} has been measured for the reaction of DMSO with ${}^\bullet OH$ radicals.[5] Such a high rate constant may exclude a direct hydrogen abstraction from the sulfoxide, as given in reaction 3, but is compatible with an addition to the sulfoxide function to give the intermediate I (reaction 2). Thus, the transient intermediate I has been postulated, although, so far, no direct experimental evidence has been presented for such a species. The dissociation of intermediate I can lead to the production of ${}^\bullet CH_3$ radicals (II) which can further abstract hydrogen from DMSO to form methane and methylsulfinic methyl radicals, ${}^\bullet CH_2SOCH_3$ (III) (reaction 4).

The reactive intermediate ${}^\bullet CH_3$ was first observed by Dixon and co-workers in their EPR flow experiments of ${}^\bullet OH$ reacting with DMSO.[6] Here, the ${}^\bullet OH$ radical was not formed by the photolysis of H_2O_2, but by mixing an aqueous solution containing the titanous ion (and H_2SO_4) with a dilute aqueous solution of H_2O_2. It has been pointed out that the results obtained in rapid-mixing experiments differ from those in the photolysis setup.[4] Thus, the outcome and the reaction pathways may be different. Other techniques, such as EPR/spin trapping experiments[7] or high-energy pulse radiolysis experiments have also been employed to study the transient intermediates of this reaction.[8,9] However, other radical intermediates I and III have remained elusive, never having been conclusively identified in an EPR experiment. Even though the intermediate III has been briefly reported as a minor product of hydrogen abstraction from DMSO by either ${}^\bullet H$ or ${}^\bullet O^-$ radicals in a pulse radioloysis/pulsed EPR study,[10] no detailed EPR study or discussion has been reported in the literature.

Here, we report the time-resolved EPR experiments on this important reaction, in order to examine the reaction pathways. We have observed the chemically induced dynamic electron polarization (CIDEP) spectra of the transient intermediates, which can be characterized as I, II, and III radicals in different time domains. We will demonstrate that the time-resolved EPR (TREPR) technique allows us to monitor the time evolution of the reaction pathways from the beginning (∼0.1 μs) to the end (several μs later), when the polarization ceases. It is known that ${}^\bullet OH$ radicals undergo very fast relaxation and have not been observed by direct EPR techniques at room temperature. The electron spin polarization observed here involves the addition reaction of ${}^\bullet OH$ radicals to DMSO (reaction 2) and the hydrogen

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abstraction reaction by $^{\bullet}CH_3$ radicals (reaction 4). The CIDEP effects in the photolytic reactions are intriguing and will be discussed in this paper.

Experimental Section

Dimethyl sulfoxide (HPLC grade) and 31% hydrogen peroxide were obtained from Kanto Chemical Co. and used as supplied. Distilled water was obtained from Cica-Merck and purified in an Iwaki UP-100 ultrapure water system by ion exchange and ultrafine filtering. All solutions were carefully deoxygenated by bubbling them with nitrogen for at least 30 min.

All transient EPR measurements were performed using a JEOL RSV2000 spectrometer without field modulation. Thoroughly deoxygenated solutions were pumped through a quartz flat cell inside a TE102 microwave cavity. The fourth harmonic of a Nd:YAG laser at 266 nm wavelength (Quanta-Ray GCR series) was employed to excite the flowing samples. Such irradiation allows the generation of $^{\bullet}OH$ radicals by the photodecomposition of H_2O_2. Even though the UV−vis spectrum of DMSO shows some absorption at 266 nm, experiments performed on DMSO alone produced no EPR signals. Transient EPR signals were collected from the spectrometer with a 500 MHz Tektronics TDS540 digital oscilloscope and were integrated within user-defined time windows on a personal computer that was off-line from the experiment. Signal averaging through repeated sampling was performed to the extent required to obtain suitable signal-to-noise ratios. In general, 12 scans were required for CIDEP spectra, and up to 10 000 scans were required for time profile of each individual peak to obtain good S/N ratios.

Results and Discussion

1. **Identification of Radicals.** *(a)* $\bullet CH_3$ *radicals.* Figure 1a shows the early time (150−250 ns, after laser excitation) EPR spectrum obtained for a 0.8 M solution of H_2O_2 in pure DMSO. A clear four-line spectrum (referred to as set A) is observed with a g value of 2.0026(±0.0002) and a hyperfine coupling constant of 2.27(±0.02) mT. The spectrum is assigned to the methyl radical (intermediate II). The observed spectral parameters are consistent with literature values for the methyl radical under similar conditions.[10,11] Indeed, this signal can be observed at a very early time (~100 ns). However, the signal is relatively broadened due to the time that is taken for the newly created magnetization to move into the observation plane.

The spectrum displayed in Figure 1a shows a clear E/A* (emissive/absorptive) polarization pattern. Such a pattern is likely produced by a mixture of single-phase and pure RPM signals. The single-phase signal is unlikely because the triplet mechanism (TM), as it is known from the literature regarding the photolysis of hydrogen peroxide, takes place from the singlet excited state.[12] Because its relative magnitude increases over time, the single-phase signal most likely arises from thermally equilibrated $^{\bullet}CH_3$ radicals. The RPM polarization is believed to come entirely from freely diffusing pairs (f-pairs). The RPM contribution is clearly asymmetric and must derive from a radical pair in which the counter radical has a g value greater than the methyl radical. Detailed discussion of the polarization pattern and the nature of the counter radical will be presented later.

In an effort to confirm the assignment of intermediate II, we performed the photochemical reaction of H_2O_2 with deuterated DMSO. Figure 2a shows the early time field sweep spectra obtained in the deuterated sample. We observe a seven-line spectrum with equal splittings between each line. The spectrum can be assigned to three equivalent deuterons coupled to an unpaired electron spin. The measured hyperfine coupling constant is 0.35(±0.003) mT, which is in complete agreement with the literature values for the $^{\bullet}CD_3$ radical.[11] Thus, we establish the identity of the four-line spectrum (set A) as $^{\bullet}CH_3$, without any ambiguity.

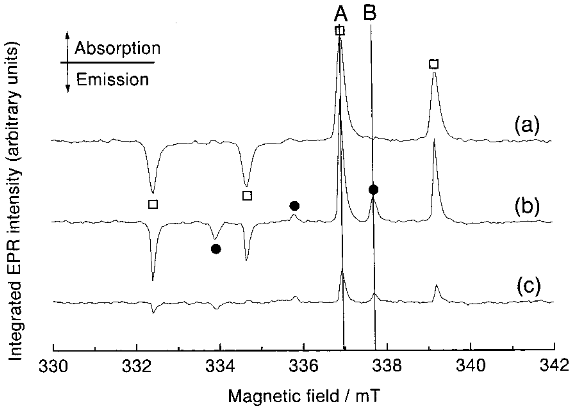

Figure 1. Transient EPR spectra for a 0.8 M solution of H_2O_2 in DMSO with time integration windows of (a) 150−250 ns, (b) 500−1000 ns, and (c) 2000−3000 ns after laser irradiation. The signal positions of sets A and B are represented by (□) and (●), respectively. Time profiles for the spectral lines A and B are illustrated in Figure 5. Spectral lines A (quartet) were assigned to the $^{\bullet}CH_3$ radical and lines B (triplet), to the $^{\bullet}CH_2SOCH_3$ radical.

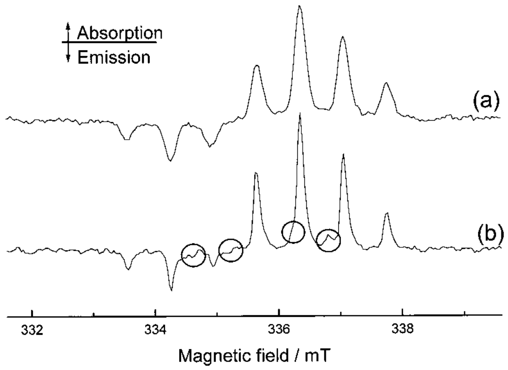

Figure 2. Transient EPR spectra for a 0.8 M solution of H_2O_2 in deuterated DMSO (CD_3SOCD_3) with time integration windows of (a) 200−400 ns and (b) 600−900 ns.

(b) $^{\bullet}CH_2SOCH_3$ *Radicals.* Figure 1b shows the spectrum of H_2O_2 with DMSO measured at a later time, 500−1000 ns after laser excitation. There is now an additional three-line signal (referred to as set B) with the same g value as the methyl radical and a hyperfine coupling constant of 1.90(±0.02) mT. The three-line spectral pattern arises from two equivalent protons coupled to an unpaired electron spin. We tentatively assign the spectrum to $^{\bullet}CH_2SOCH_3$, methylsulfinic methyl radical (intermediate III). Indeed, this species has previously been observed with comparable magnetic parameters.[10,11]

The deuterated DMSO system further provides confirmation on the spectral assignment of intermediate III. Figure 2b shows a spectrum observed at later time in this system. Although more difficult to see, due to spectral overlap, additional lines are present (marked with circles). They represent four lines of a five-line spectrum (from two equivalent deuterons) with the hyperfine coupling constant 0.28(±0.003) mT. This is in excellent agreement with the expected value calculated from the protonated system, a factor of $a_H/a_D = 6.7$.

We further investigated the individual lines of set B, using a much reduced magnetic field sweep width. The high-field line is illustrated in Figure 3. We observed the line was split into a

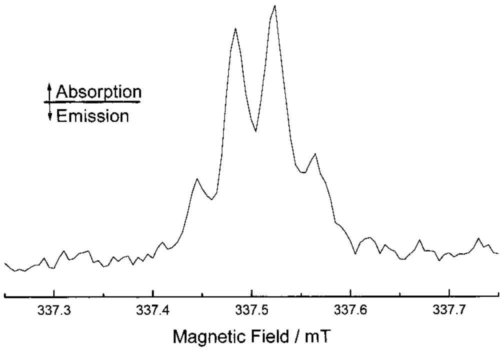

Figure 3. 0.5 mT field sweep EPR spectrum of line B from Figure 1. The line is clearly split into a quartet pattern with an approximate intensity ratio of 1:3:3:1 from the methyl protons in $^\bullet CH_2SOCH_3$.

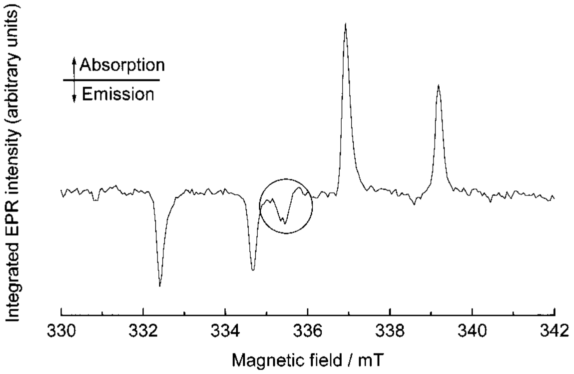

Figure 4. Transient EPR spectrum for a solution of 0.08 M H_2O_2 in DMSO with a time integration window of 100−300 ns. The highlighted additional central, emissive peak has a *g* value of 2.0050(±0.0003) and is tentatively assigned to radical intermediate I, $(CH_3)_2SO(OH)^\bullet$.

quartet pattern with approximate relative magnitudes of 1:3:3:1. The quartet pattern can be ascribed to three equivalent protons of the methyl group of $^\bullet CH_2SOCH_3$ with $a_H = 0.04$ (±0.002) mT. The study of deuterated sample and the observation of quartet structure from one of the proton lines allow unequivocal assignment of the set B lines to $^\bullet CH_2SOCH_3$ radicals.

The assignment of set B to the methylsulfinic methyl radical is further supported by the fact that this three-line spectrum is formed later in time than the methyl radical, which is consistent with the hydrogen abstraction reaction by methyl radical from the parent DMSO (see reaction 4). At time long after the laser excitation, the polarized signal becomes much smaller as the system approaches equilibrium. This results in the inversion of some of the spectral lines, as the RPM polarization decreases relative to the equilibrium signal (see Figure 1c).

(c) $(CH_3)_2SO(OH)^\bullet$ and Other Radicals. In an attempt to establish a signal attributable to radical intermediate I, according to reaction 2, we examined the very early time signal. A weak, broad signal is barely discernible in Figure 1a. However, we obtained a better spectrum at the early time interval of 100−300 ns for a dilute solution of 0.08 M H_2O_2 in pure DMSO (Figure 4). We observed an *emissive* peak at a low-field shifted position, whose identity is not obvious. This peak was slightly apparent at higher concentrations of H_2O_2, but was more readily observed under dilute conditions. The calculated *g* value for this peak is 2.0050(±0.0003). Comparison with literature values of radicals similar to I reveals that the radical $CH_3SO_2^\bullet$ has a *g* value of 2.0049 and has sulfur in the same pentavalent state bound to two oxygen atoms, as in $(CH_3)_2SO(OH)^\bullet$ (intermediate I).[11] On the basis of this comparison and the appearance of this peak at an early time only, we tentatively assign this broad peak to the intermediate I as proposed in reaction 2. The nonsymmetric nature of the methyl radical polarization, discussed earlier, necessitates a counter radical with a *g* value greater than that of the methyl radical. Thus, one obvious candidate in this system is intermediate I.

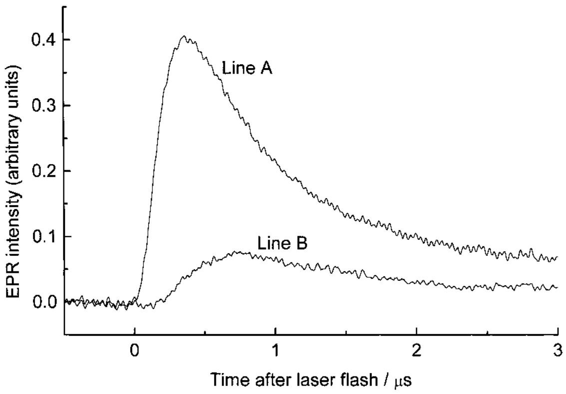

Figure 5. Time profiles for spectral lines A and B from Figure 1. Signal B clearly appears much later than signal A, consistent with the formation of the radical species in a subsequent reaction.

It has been reported that $^\bullet CH_3$ can react with oxygen molecules to form methyl peroxy radicals.[1] In one of our experiments, the sample was intentionally bubbled with O_2 for 30 min and throughout the EPR experiment, but we failed to observe a signal that can be assigned to peroxy radicals within our experimental time window. However, it is known that oxygen-containing peroxy radicals could give rise to a broad line because of rapid relaxation, which may prevent direct detection by EPR of peroxy radicals at room temperature. Furthermore, when experiments are performed at high concentrations of H_2O_2, other complications can also arise: [4]

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O \qquad (5)$$

However, we have not detected any transient species that can be assigned to the spin adducts arising from the reaction of $HO_2^\bullet$ with other substrates.

2. **Polarization Patterns and Reaction Mechanism.** The time profiles of the lines of sets A ($^\bullet CH_3$) and B ($^\bullet CH_2SOCH_3$) are further illustrated in Figure 5. The peak intensity of set B clearly occurs at a later time than that of set A. This is further evidence against the pathway of hydrogen abstraction by $^\bullet OH$ from DMSO (reaction 3). To further support the three-line signal being attributed to the methylsulfinic methyl radical (III) formed by reaction 4, we performed another set of EPR experiments on an equimolar mixture of 0.8 M H_2O_2/0.8 M DMSO in deionized water instead of the pure DMSO used previously. Figure 6 shows the time-resolved EPR spectrum obtained from such an aqueous solution with a much reduced DMSO concentration. The time window is identical to that in Figure 1b. However, here the three-line signal intensity (set B) is drastically reduced, if present at all. The results indicate that the three-line signal strength (proportional to the concentration of intermediate III) critically depends on the DMSO concentration. This is consistent with a species formed in a two-step process, with both steps involving interaction with a DMSO molecule. Again, we can rule out the occurrence of reaction 3 based on the time profile of spectral lines displayed in Figure 5.

Further examination of Figure 1 reveals that the methyl radicals are formed immediately after the laser flash, within the time resolution of our spectrometer. More significantly, however, the methyl radical exhibits a polarized signal for a much longer

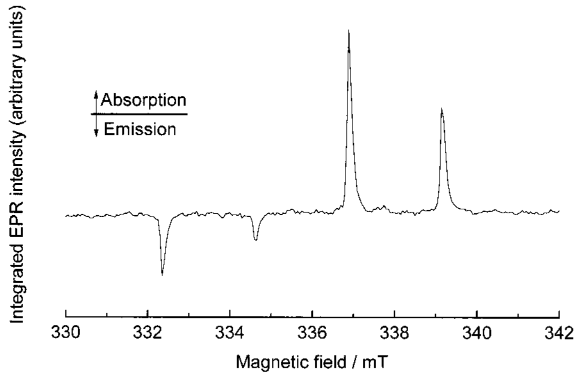

Figure 6. Transient EPR spectrum for an equimolar solution of 0.8 M H_2O_2 and DMSO in water. The time integration window is identical to Figure 1b. Note that the set B lines are virtually unobservable in this spectrum.

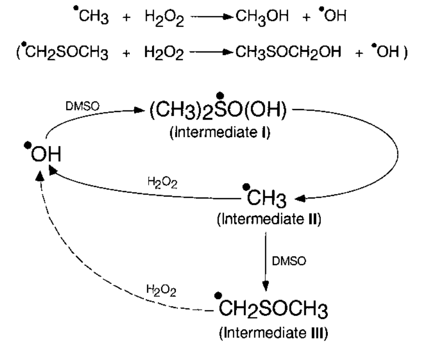

Figure 7. Proposed cyclic mechanism for the regeneration of $^•CH_3$ f-pair polarization throughout the reaction period.

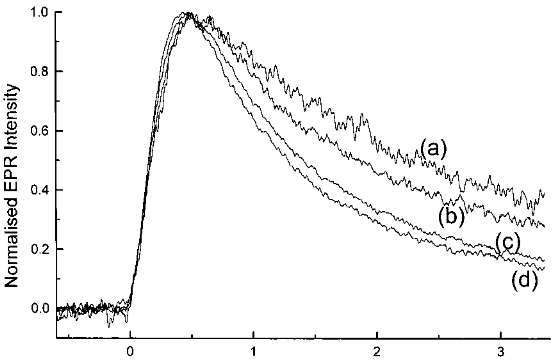

Figure 8. Variation of the time profile of $^•CH_3$ radical (line A in Figure 1) with H_2O_2 concentration. The H_2O_2 concentrations are (a) 0.08 M, (b) 0.16 M, (c) 0.8 M, and (d) 4.0 M.

period of time than expected, based on its known T_1 relaxation time (200 ns).[10] The observation of such a long-lived polarized signal implies that methyl radicals are not just generated in the initial reaction process but are regenerated throughout the time period where polarization is observed. We thus propose that the regeneration is a result of the continuous reaction of one of the product radicals (methyl or methylsulfinic methyl) with an H_2O_2 molecule. The proposed reaction scheme is shown in Figure 7. To examine such an effect, we performed experiments as a function of hydrogen peroxide concentrations. Figure 8 shows the time profile of $^•CH_3$ line at various peroxide concentrations. At higher concentrations, the rate of polarization decay of the methyl line is increased, a bimolecular process, consistent with the mechanism illustrated in Figure 7. Note that the overall signal intensity increases substantially with peroxide concentration.

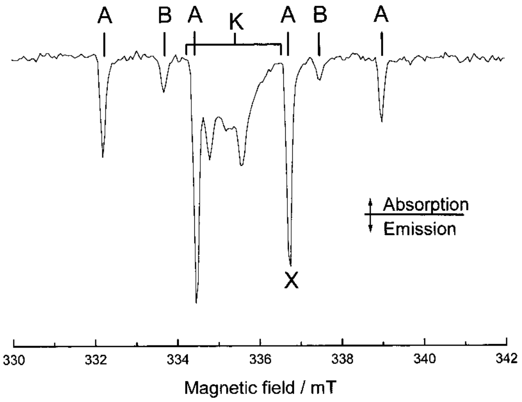

Figure 9. Transient EPR spectrum (time window = 300−500 ns) obtained from the reaction of photoexcited benzophenone (0.01 M) with DMSO. Spectral line designations are K, $Ph_2C(OH)^•$ (benzophenone ketyl), A, $^•CH_3$ and B, $^•CH_2SOCH_3$ radicals. The transient decay of line X ($^•CH_3$) is given in Figure 10b.

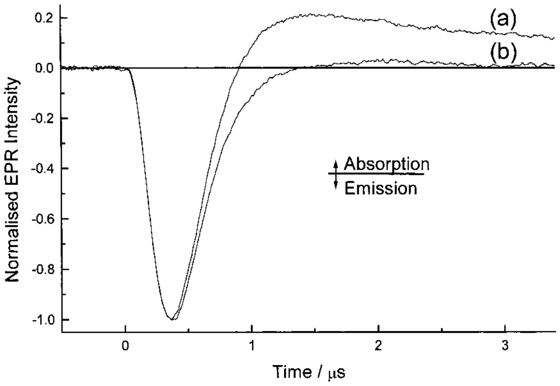

Figure 10. Time profiles for the decay of the high-field $^•CH_3$ line (line X in Figure 9) produced by the reaction of benzophenone (0.01 M) with DMSO in the (a) presence and (b) absence of H_2O_2 (0.08 M). The strong signal inversion in curve (a) is attributed to f-pair polarization derived from the reaction of $CH_3^•$ with H_2O_2 (see text).

Even stronger evidence for this reaction pathway was provided from experiments involving the photochemical reaction of benzophenone (0.01 M) with DMSO. We performed this reaction in the presence and absence of H_2O_2, using the third harmonic of the Nd:YAG laser (355 nm). Note that 355 nm can excite benzophenone to the lowest triplet state to initiate the photochemical reaction, but it cannot excite H_2O_2 to an upper electronic state. Upon laser photolysis, the system rapidly produces benzophenone ketyl, methyl, and methylsulfinic methyl radicals. Figure 9 shows a typical spectrum obtained in this system. The details of the photochemical reactions of benzophenones with DMSO will be published elsewhere.[13] All three of the radicals mentioned above are clearly observable and possess TM polarization arising from the initial benzophenone triplet state. Figure 10 shows the time profiles of the methyl line (marked X in Figure 9) in the presence (Figure 10a) and absence (Figure 10b) of hydrogen peroxide. When H_2O_2 is absent, the methyl signal decays rapidly with a lifetime of 200 ns, in excellent agreement with literature values of the T_1 relaxation time.[10] There is a small absorptive equilibrium signal visible at later time. In the presence of hydrogen peroxide, however, the signal turns over from its initially emissive TM polarization, to absorptive RPM (Figure 10a). The results indicate that hydrogen peroxide reacts with radicals to regenerate methyl radicals.

To identify whether the attacking species is the $^•CH_3$ or the $^•CH_2SOCH_3$ radical, we reexamine the time profiles for $^•CH_3$ radical (line A, Figure 1a) and the corresponding line from

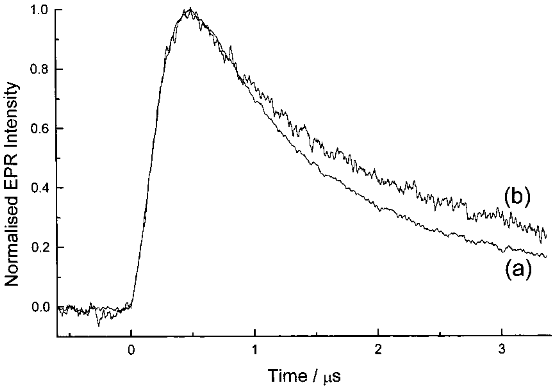

Figure 11. Time profiles for the decay of the high-field $^{\bullet}CH_3$ line (line A in Figure 1) for solutions of 0.8 M H_2O_2 in (a) pure DMSO and (b) 0.8 M DMSO in H_2O.

Figure 6, in which dilution with water has removed almost all signal due to $^{\bullet}CH_2SOCH_3$ radical. The time profiles of these two samples are displayed in Figure 11. Although there is a slight change in the kinetics, because of the change in the DMSO concentration, the effect is much too small to indicate whether methylsulfinic methyl radical were the radical reacting with H_2O_2. From this indirect evidence, it appears likely that the methyl radical is responsible for the reaction with H_2O_2 and thus engages its own regeneration. Such a mechanism can lead to the generation of methanol (see Figure 7). The results are consistent with the product analysis studies in which formaldehyde has been identified as a reaction product.[1] It appears likely that even in the absence of molecular oxygen, formaldehyde could be produced from methanol under these oxidizing conditions.

Simulations were performed in an attempt to reproduce the observed polarization patterns of methyl radicals. We were not able to reproduce a fit for all four methyl lines using a mixture of single phase (ratio 1:3:3:1) and RPM signals, regardless of the extent of mixing and g value difference between the radical pair members. Similarly, early time spectra (for which it is assumed that the polarization is entirely RPM) could not be reproduced accurately. Simulations do reveal that the counter radical to $^{\bullet}CH_3$ must possess a significantly larger g value. Two possible candidates for the counter radicals are intermediate I and the hydroxyl radical (whose g value in such a solution is uncertain, but the reported values at low temperatures are much greater than that of the methyl radical[11]). However, the hydroxyl radical is not observable in solution and its participation in any radical pair would destroy polarization; we therefore believe that the most likely candidate for the counter radical is intermediate I, which, like hydroxyl, can produce methanol through a singlet-reaction pathway. This is further strengthened by the fact that methyl radicals are created in the unimolecular decay of intermediate I. This RP is consistent with the proposed cyclic reaction mechanism given in Figure 7, as this pair would be regenerated in a similar process at later times.

It is believed that the error in calculated intensity ratios may be attributed to moderately fast relaxing counter radicals, as described in a recent paper by Eveson et al.[14] We have not attempted to employ such techniques to simulate our spectra, as they are applicable only to signals arising from the geminate phase of RPM spin polarization. It is possible that our results may prove to make an excellent case for an extension of their theory to include contribution from f-pair radical encounters.

Conclusion

This study has provided a wealth of new information on the intermediates and kinetic processes involved in the photochemical reaction between H_2O_2 and DMSO. Unequivocal identification of two of the reaction intermediates, along with their formation sequence, has been established. An EPR signal tentatively ascribed to intermediate I was also observed. No signal due to the $^{\bullet}OH$ radical was observed in this study, likely because of its fast relaxation time and high reactivity.[15] However, it is likely that its presence may exert some effects on the polarization pattern of the methyl radicals, which under suitable experimental conditions may reveal information on its relaxation rate and g value.

Finally, we verify, experimentally, a proposed cyclic mechanism in which $^{\bullet}CH_3$ radicals attack H_2O_2 molecules, leading to the regeneration of $^{\bullet}CH_3$ radicals. The cyclic regeneration pathway allows the polarized $^{\bullet}CH_3$ signal to be observed several μs after the initiation of the photochemical reaction (at least 1 order of magnitude longer than the T_1 value of $^{\bullet}CH_3$). Subsequently, the f-pair RPM polarization of $^{\bullet}CH_3$ radicals can be observed throughout the entire course of the photochemical reaction.

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