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Kinetic Model for Determination of Reaction and Polarization Dynamics from Chemically Induced Electron Spin Polarized Electron Spin Resonance Spectra

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The dynamics of photochemical reactions exhibiting chemically induced electron spin polarization (CIDEP) are modeled by kinetic equations that include all relevant parameters, including reaction of the excited precursor as both a singlet and a triplet and spin exchange during radical encounters. Analysis of the acetone/2-propanol photolysis reveals spin exchange effects and provides further evidence that the anomalous net electron spin resonance (ESR) absorption of the 2-propanolyl radical is due to spin−lattice relaxation in the triplet acetone precursor. The weakening of this net absorption in acetone/triethylamine photolyses is due to the rapid reaction of photoexcited acetone with triethylamine resulting in reaction via both its singlet state, which cannot produce a net polarization, and its triplet state, which yields no triplet polarization and reacts before spin−lattice relaxation can produce full equilibrium polarization.

Introduction

Chemically induced electron spin polarizations (CIDEPs), observed in the electron spin resonance (ESR) spectra of the free radical products of many photochemical and other energetically initiated reactions, contain a wealth of important information about the reaction precursors and the subsequent reaction dynamics, as well as the polarization and spin relaxation mechanisms.[1,2] Not surprisingly, however, extraction of these data from the observed spectra can be severely challenged by the corresponding complexity of these reaction systems and the presence of multiple polarization and spin relaxation mechanisms operating on different time scales. For example, the apparently simple photolysis of acetone in 2-propanol has been the subject of a decades long and still incompletely resolved controversy over the origin of a net absorption superimposed on the emission/absorption CIDEP spectrum predicted by the radical pair mechanism (RPM) for a pair of identical 2-propanolyl radicals.[3−13]

Usually, CIDEP spectra are analyzed by comparison with spectra calculated from models whose equations contain the physically significant quantities as adjustable parameters. This requires spectra determined over as wide a range of times as possible, as various aspects of the reaction and polarization dynamics have markedly different time dependences. Although older continuous wave (CW) ESR investigations have yielded some useful results,[1,2] pulsed methods such as Fourier transform (FT) ESR provide better sensitivity and time resolution over wider intervals and also avoid the complication of having the system exposed to a microwave field prior to the time of measurement.[2,14−16] Recent FT investigations have confirmed the power of this method for a number of interesting reaction systems,[2,16,17] including various acetone photolyses.[9,10] Investigations to date have focused primarily on kinetic parameters such as the reaction rate of the excited precursor and the bimolecular recombination and spin−lattice relaxation rates.

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Other interesting, but less investigated, aspects of these systems are the magnitudes of the polarizations, whether the excited precursor reacts as a singlet, as a triplet, or via both channels, and the role of spin exchange during radical encounters. All of these features will be considered here, using a comprehensive set of kinetic equations to model and analyze the experimental data.

Kinetic Model

Derivation of the rate equations for a CIDEP-yielding reaction initiated by an excited precursor is simplified by assuming that two chemically identical radicals are produced initially. The case where the initial reaction produces different radicals can be treated by multiplying the final results by the fractional concentration of the radical of interest as the ESR intensities are unaffected by the interaction of identical radicals in the same nuclear spin state. Although the parameters determined by this model for multiradical systems are averages over the different radicals and their interactions, these differences usually are not large enough to be a problem. If need be, theory can aid in breaking down the averaged parameters into contributions from the individual radicals.

Thus, a general CIDEP-producing reaction scheme initiated by photoexcitation of a precursor P and its reaction with a solution molecule S to yield a radical pair is

$$\mathrm{P} \xrightarrow{h\nu} {}^1\mathrm{P}^* \begin{cases} +\mathrm{S} \xrightarrow{{}^1k} {}^1\overline{\mathrm{R}^\bullet_M\ \mathrm{R}^\bullet_{M'}} \rightarrow \mathrm{R}^\bullet_M\ldots\mathrm{R}^\bullet_{M'} \\ \xrightarrow{k_{\mathrm{isc}}} {}^3\mathrm{P}^* + \mathrm{S} \xrightarrow{{}^3k} {}^3\overline{\mathrm{R}^\bullet_M\ \mathrm{R}^\bullet_{M'}} \rightarrow \mathrm{R}^\bullet_M\ldots\mathrm{R}^\bullet_{M'} \end{cases} \tag{1a}$$

$$\mathrm{R}^\bullet_{\beta/\alpha,M} + \mathrm{R}^\bullet_{\alpha/\beta,M'} \xrightarrow{k_{\mathrm{ex}}} \mathrm{R}^\bullet_{\alpha/\beta,M} + \mathrm{R}^\bullet_{\beta/\alpha,M'}\ \text{(spin exchange)} \tag{1b}$$

$$\mathrm{R}^\bullet_{\beta/\alpha,M} + \mathrm{R}^\bullet_{\alpha/\beta,M'} \xrightarrow{k_{\mathrm{e}}} \begin{cases} \text{products} \\ {}^{\mathrm{F}}\overline{\mathrm{R}^\bullet_M\ \mathrm{R}^\bullet_{M'}} \rightarrow \mathrm{R}^\bullet_M\ldots\mathrm{R}^\bullet_{M'} \end{cases} \tag{1c}$$

where $\mathrm{R}^\bullet_{\beta/\alpha,M}$ denotes a radical in the down/up electron spin states with nuclear spin state M. These reactions can yield a polarized ESR spectrum from a combination of the triplet mechanism[1b,18] (TM) and spin−lattice relaxation in the triplet precursor,[3] and RPM polarization[1b,19,20] in the radical pairs ${}^S\overline{\mathrm{R}^\bullet_M\ \mathrm{R}^\bullet_{M'}}$, where $S = 1$ or 3 indicates, respectively, a geminate singlet or triplet pair, and F denotes a free pair formed by the random encounter of separated radicals. Here, ${}^1k$ and ${}^3k$ are the rates of reaction of the excited singlet (${}^1\mathrm{P}^*$) and triplet (${}^3\mathrm{P}^*$) precursor states with S, k_{isc} is the rate of the intersystem crossing from ${}^1\mathrm{P}^*$ to ${}^3\mathrm{P}^*$, and k_{ex} and k_{e} are the rate constants for radical encounters at the spin exchange separation (r_{ex}) and the reaction separation (r_{e}), respectively, where it is expected that $k_{\mathrm{ex}} > k_{\mathrm{e}}$.[21]

In the derivation of the rate equations for the ESR intensity produced by the foregoing reaction scheme and the accompanying polarization processes, a useful simplification is to assume that both the singlet and triplet reactions in eq 1a produce radicals at the same rate k_{f}. This approximation is reasonable as this rate usually is determined by the time constant of the experiment (ca. 10 ns),[10,16] which can resolve ${}^3k$ in some cases but not ${}^1k$ if it is fast enough to compete with intersystem crossing, which requires about ${}^1k > 0.1k_{\mathrm{isc}}$. With this simplification the radical concentration (N) is determined by the equation

$$\mathrm{d}N/\mathrm{d}t = 2k_{\mathrm{f}}N_0\mathrm{e}^{-k_{\mathrm{f}}t} - \frac{1}{4}p_{\mathrm{S}}k_{\mathrm{e}}N^2 \tag{2}$$

where N_0 is the initial excited precursor concentration, and the factor ${}^1/_4 p_{\mathrm{S}}$ comes from the encounter rate of opposite-spin radicals being ${}^1/_4 k_{\mathrm{e}}N^2$, of which ${}^1/_2$ have singlet character and recombine with probability p_{S} to eliminate two radicals. Since the radical production rate k_{f} is much faster than their bimolecular recombination, one obtains a satisfactory solution of eq 2,

$$N(t) \cong 2N_0(1 - \mathrm{e}^{-k_{\mathrm{f}}t})\Big/\left(1 + \frac{1}{2}p_{\mathrm{S}}k_{\mathrm{e}}N_0t\right) \tag{3}$$

by taking the initial radical concentration to be $2N_0(1 - \mathrm{e}^{-k_{\mathrm{f}}t})$ and further approximating this as $2N_0$ in the denominator of eq 3.

Similarly, the initial production of spin-polarized radicals by the reactions in eq 1a is used as the initial condition in solving the differential equations for the subsequent slower processes of relaxation in the separated radicals, spin exchange, recombination, and the accompanying F-pair polarization. With the aforementioned simplification of treating radical formation via both the singlet and triplet channels as occurring at rate k_{f}, solution of the differential equations describing polarized radical production in eq 1a yields the following expression for the initial ESR intensity of the Mth hyperfine line:

$$\begin{aligned} S_M(t \approx 0) = {} & \\ & 2I_MN_0\left\{f_{\mathrm{T}}\left[\frac{{}^3k}{{}^3k + {}^3W}\left(\rho_{\mathrm{TM}} - \frac{2}{3}\rho_{\mathrm{eq}}\right)(1 - \mathrm{e}^{-(k_{\mathrm{f}}+{}^3W)t}) + \right.\right. \\ & \left.\left. \frac{2}{3}\rho_{\mathrm{eq}}(1 - \mathrm{e}^{-k_{\mathrm{f}}t})\right] + \left[-\frac{1}{3}f_{\mathrm{T}} + (1 - f_{\mathrm{T}})\right]\rho_M^{\mathrm{ST_0}}(1 - \mathrm{e}^{-k_{\mathrm{f}}t})\right\} \end{aligned} \tag{4}$$

Here, $S_M = N_{\beta,M} - N_{\alpha,M}$, where $N_{\beta/\alpha,M}$ is the concentration of $\mathrm{R}^\bullet_{\beta/\alpha,M}$, I_M is the statistical weight of the Mth nuclear spin state, and $f_{\mathrm{T}} = k_{\mathrm{isc}}/(k_{\mathrm{isc}} + {}^1k)$ and $(1 - f_{\mathrm{T}})$ are the fractions of the reaction occurring through the triplet and singlet channels. The first term in eq 4 is the net polarization developed in the triplet; it is a combination of the TM polarization ρ_{TM}, calculated as described in refs 1b and 18, and the thermal equilibrium polarization $\rho_{\mathrm{eq}} = g\mu_{\mathrm{B}}H/(kT)$ which replaces it at the triplet spin−lattice relaxation rate (${}^3W$) prior to reaction of the triplet.[3] The second term is the RPM polarization of the Mth hyperfine state, where $\rho_M^{\mathrm{ST_0}}$, calculated as described in refs 19 and 20, has the weight factor of $-{}^1/_3$ for the triplet, where only the $\mathrm{T_0}$ level is polarized, and unity for the singlet. Equation 4 shows that, if the time-resolution capability of the experiment permits, the TM contribution can be distinguished from other contributions to S_M on the basis of their different growth rates.[9,17] For simplicity, this possibility is neglected here, and eq 4 becomes

$$S_M(t \approx 0) = 2I_MN_0\left[f_{\mathrm{T}}\rho_{\mathrm{T}} + \left(1 - \frac{4}{3}f_{\mathrm{T}}\right)\rho_M^{\mathrm{ST_0}}\right](1 - \mathrm{e}^{-k_{\mathrm{f}}t}) \tag{5}$$

where

$$\rho_{\mathrm{T}} = \left({}^3k\rho_{\mathrm{TM}} + \frac{2}{3}{}^3W\rho_{\mathrm{eq}}\right)\Big/({}^3k + {}^3W) \tag{6}$$

Following its initial rapid development, S_M evolves under the influence of spin−lattice relaxation, spin exchange, and F-pair polarization and eventually is lost to radical recombination, the last three effects occurring during radical encounters. The rate equations describing these effects, where the parts due to spin exchange, reaction, and F-pair polarization are derived in the Appendix, are

$$\frac{\mathrm{d}S_M}{\mathrm{d}t} = -W\left(S_M - \frac{1}{2}\rho_{\mathrm{eq}}I_M N\right) - k_{\mathrm{ex}}(N_{\beta,M}N_\alpha - N_{\alpha,M}N_\beta) - \frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}\rho_M^{\mathrm{ST}_0}(N_{\alpha,M}N_\beta + N_{\beta,M}N_\alpha) \quad (7)$$

where W ($W = 1/T_1$) is the radical spin−lattice relaxation rate, and N_α and N_β are the concentrations of radicals with "up" and "down" electron spins. It is to be noted that F-pair RPM polarization is the only direct effect of recombination on the population difference between spin states as recombination itself leads to equal loss of both spin states, although its decreasing of the net radical concentration combined with relaxation does lead to eventual decay of the ESR signals.

The usual analysis of the experimental data separates it into the symmetric and antisymmetric components: $\sum S_M = {}^1/_2(S_M + S_{-M})$ and $\Delta S_M = {}^1/_2(S_M - S_{-M})$. This greatly simplifies the rate equations in the usual situation where hyperfine interactions dominate the ST$_0$ mixing and $\rho_M^{\mathrm{ST}_0} = -\rho_{-M}^{\mathrm{ST}_0}$. Then $\sum S_M$ is a pure absorption or emission, that is, $\sum S_M \propto I_M$ and is unaffected by either ST$_0$ RPM polarization or exchange interactions, whereas ΔS_M is due exclusively to the ST$_0$ polarization. The rate equations for $\sum S_M$ and ΔS_M are

$$\frac{\mathrm{d}\sum S_M}{\mathrm{d}t} = -W\left(\sum S_M - \frac{1}{2}\rho_{\mathrm{eq}}I_M f_{\mathrm{R}}N\right) \quad (8a)$$

$$\frac{\mathrm{d}\Delta S_M}{\mathrm{d}t} = -\left(W + \frac{1}{2}k_{\mathrm{ex}}N\right)\Delta S_M - \frac{1}{4}k_{\mathrm{e}}p_{\mathrm{S}}I_M\rho_M^{\mathrm{ST}_0}f_{\mathrm{R}}N^2 \quad (8b)$$

where, as discussed previously, f_{R} is the fraction of the ESR-observed radical.

The solution of eq 8a for $\sum S_M$, where N is given by eq 3 with $(1 - \mathrm{e}^{k_{\mathrm{f}}t}) \cong 1$, which is valid for $k_{\mathrm{f}} \gg W$ and ${}^1/_2k_{\mathrm{e}}p_{\mathrm{S}}N$, is

$$\sum S_M(t) = 2I_M f_{\mathrm{R}}N_0\left[f_{\mathrm{T}}\rho_{\mathrm{T}}(1 - \mathrm{e}^{-k_{\mathrm{f}}t}) + \frac{1}{2}\rho_{\mathrm{eq}}W\int_0^t \frac{\mathrm{e}^{W\tau}}{1 + \frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}N_0\tau}\,\mathrm{d}\tau\right]\mathrm{e}^{-Wt} \quad (9)$$

$$\approx 2I_M f_{\mathrm{R}}N_0\left[f_{\mathrm{T}}\rho_{\mathrm{T}}(1 - \mathrm{e}^{-k_{\mathrm{f}}t})\mathrm{e}^{-Wt} + \frac{1}{2}\rho_{\mathrm{eq}}\left(\frac{1}{1 + \frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}N_0 t} - \mathrm{e}^{-Wt}\right)\right]$$

Here, the first term is the initial net absorption or emission from the triplet given by eq 5, and the second term is due to spin−lattice relaxation in the separated radicals. The approximation to the integral is strictly valid only at long times ($t \gg 1/W = T_1$), where the spin states are thermally equilibrated, and short times (${}^1/_2k_{\mathrm{e}}N_0t \ll 1$), while at intermediate times its error is approximately proportional to ${}^1/_2k_{\mathrm{e}}p_{\mathrm{S}}N_0/W$. This can lead to large errors in the value of W determined by fitting to the experimental $\sum S_M$ and consequently to great difficulties in obtaining satisfactory fits to ΔS_M. Nonetheless, the approximation is useful because, as discussed later, its simplicity in the long-time region makes this a good place to begin the fitting process.

The solution to eq 8b for ΔS_M, with the initial ST$_0$ polarization given by eq 5, is

$$\Delta S_M(t) = 2I_M f_{\mathrm{R}}\rho_M^{\mathrm{ST}_0}\left[\left(1 - \frac{4}{3}f_{\mathrm{T}}\right)(1 - \mathrm{e}^{-k_{\mathrm{f}}t})N_0 - \frac{1}{8}k_{\mathrm{e}}p_{\mathrm{S}}\int_0^t N^2 \exp\left(\int_0^\tau\left(W + \frac{1}{2}k_{\mathrm{ex}}N\right)\mathrm{d}u\right)\mathrm{d}\tau\right] \times \exp\left(-\int_0^t\left(W + \frac{1}{2}k_{\mathrm{ex}}N\right)\mathrm{d}\upsilon\right) \quad (10)$$

Substituting for N, using eq 3 with $(1 - \mathrm{e}^{-k_{\mathrm{f}}t}) \cong 1$ as before, and carrying out the integrations in the exponential factors give

$$\Delta S_M(t) = 2I_M f_{\mathrm{R}}N_0\rho_M^{\mathrm{ST}_0}\left[\left(1 - \frac{4}{3}f_{\mathrm{T}}\right)(1 - \mathrm{e}^{-k_{\mathrm{f}}t})\frac{\mathrm{e}^{-Wt}}{\left(1 + \frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}N_0t\right)^{2k_{\mathrm{ex}}/(k_{\mathrm{e}}p_{\mathrm{S}})}} - \frac{\frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}N_0}{\left(1 + \frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}N_0t\right)^2 W}\int_0^t\left(\frac{1 + \frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}N_0\tau}{1 + \frac{1}{2}k_{\mathrm{e}}p_{\mathrm{S}}N_0t}\right)^{2[(k_{\mathrm{ex}}/(k_{\mathrm{e}}p_{\mathrm{S}}))-1]} W\mathrm{e}^{W(\tau - t)}\,\mathrm{d}\tau\right] \quad (11)$$

Similarly to the integral in eq 9, this integral approaches $(1 - \mathrm{e}^{-Wt})$ if $(k_{\mathrm{ex}} - k_{\mathrm{e}}p_{\mathrm{S}})N_0/W \ll 1$, but this condition often is not met, in which case the integral has to be evaluated numerically.

Results and Discussion

A systematic approach to fitting eqs 9 and 11 to experiment is to begin with $\sum S_M(t)$ in the long-time region where $\mathrm{e}^{-Wt} \approx 0$ and the approximation to the integral in eq 9 applies, giving $I_M/\sum S_M(t) \cong (1 + {}^1/_2k_{\mathrm{e}}p_{\mathrm{S}}N_0t)/(f_{\mathrm{R}}N_0\rho_{\mathrm{eq}})$. Thus, a simple linear fit determines the parameters $f_{\mathrm{R}}N_0\rho_{\mathrm{eq}}$ and ${}^1/_2k_{\mathrm{e}}p_{\mathrm{S}}N_0$, although it should be borne in mind that the $\sum S_M$ values, which usually are the difference of two larger quantities, may be of limited accuracy in this region of weak ESR signals. Nonetheless, with estimates of these parameters in hand, the parameters $f_{\mathrm{T}}\rho_{\mathrm{T}}$ and k_{f} can be estimated by fitting to the early-time values of $\sum S_M$, which are given by the first term in eq 9 with $\mathrm{e}^{-Wt} \approx 1$. The parameter W can then be obtained by a trial and error fit over the entire range of $\sum S_M$ values. The remaining parameters f_{T}, $k_{\mathrm{ex}}/(k_{\mathrm{e}}p_{\mathrm{S}})$, and $\rho_M^{\mathrm{ST}_0}$ can then be obtained by a trial and error fit to the ΔS_M data. The fitting criterion is the best least-squares fit to the combined $\sum S_M$ and ΔS_M data, it usually being necessary to recycle the calculation a number of times with some variation of the values of $f_{\mathrm{R}}N_0\rho_{\mathrm{eq}}$ and ${}^1/_2k_{\mathrm{e}}p_{\mathrm{S}}N_0$, as it can happen that a rather wide range of parameter values will give comparable fits to $\sum S_M$ but will differ considerably in goodness of fit to the ΔS_M data. Furthermore, the accuracy of the results is limited somewhat by the tendency of the least-squares minima to be rather broad with respect to some parameters, especially the spin−lattice relaxation (W) and spin exchange ($k_{\mathrm{ex}}/(k_{\mathrm{e}}p_{\mathrm{S}})$) parameters which can compensate each other to a considerable degree. For example, in the acetone-d_6/2-propanol-d_8 system, values of $k_{\mathrm{ex}}/(k_{\mathrm{e}}p_{\mathrm{S}})$ in the range of 1.6−2.0 with a corresponding range for T_1 of 3.0−3.8 μs yield fits of virtually equal quality. The range of possible $k_{\mathrm{ex}}/(k_{\mathrm{e}}p_{\mathrm{S}})$ values is even broader for the acetone/triethylamine systems where the results are relatively insensitive to spin exchange because of the rapid radical relaxation rate. Nonetheless, these results confirm the presence

TABLE 1: Parameters Obtained by Fitting CIDEP Spectra Obtained from Several Acetone Photolysis Systems

	acetone-d_6 in 2-propanol-d_8[a]	acetone (1 M) in triethylamine[b]	acetone (1 M) and triethylamine (1 M) in benzene[b]
$f_R N_0 \rho_{eq}$ (au)	6.3	4.8	9.6
$^1/_2 k_e p_S N_0$ (s^{-1})	1.0×10^5	5.8×10^4	1.1×10^5
k_f (s^{-1})	4.2×10^6	4.1×10^7	3.9×10^7
$k_{ex}/(k_e p_S)$	1.8	1.4	1.1
$T_1 = 1/W$ (μs)	3.4	1.0	0.81
f_T	1.0	0.56	0.86
$2\rho_T/\rho_{eq}$	1.3	0.20	0.54
$\rho^{ST_0}_{1,2,3}/\rho_{eq}$	3.5, 6.9, 10.6	9.3, _, _	9.5, _, _

[a] Data from ref 9. [b] Data from ref 10. Dashes represent no data available.

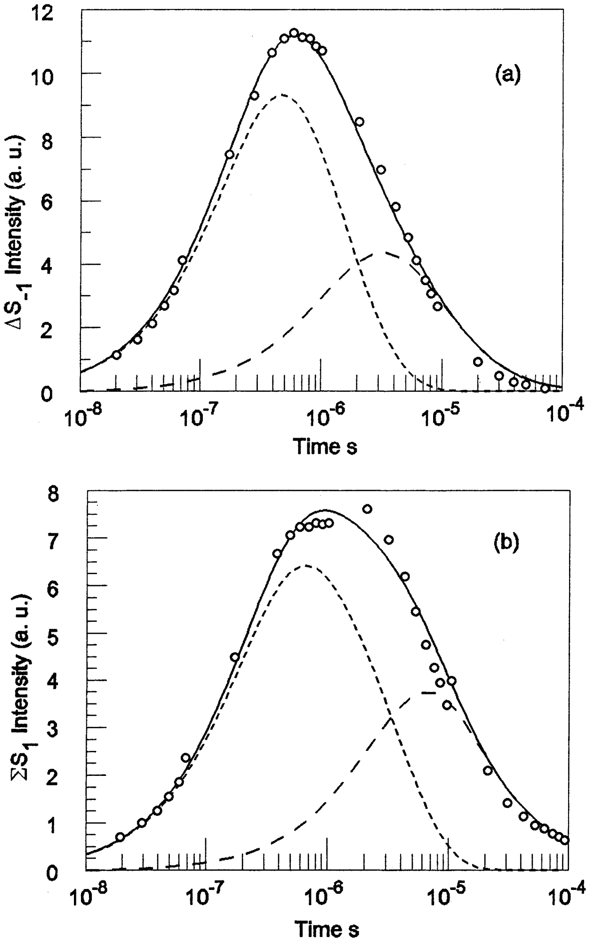

Figure 1. Least-squares fits to observed FT ESR spectra from the laser flash photolysis of acetone-d_6 in 2-propanol-d_8. (a) Difference of the amplitudes of the -1 and $+1$ hyperfine lines (ΔS_{-1}); $\Delta S_{-1} > 0$ corresponds to E/A polarization. (b) Sum of the amplitudes of the -1 and $+1$ hyperfine lines (ΣS_1). In both cases the solid line (–) is the total least-squares fit, the small-dashed line (- - -) is from triplet reaction, the large-dashed line (— — —) is from separated radicals, and the experimental values (○) are from ref 9.

of spin exchange and its importance in accounting for the RPM polarizations, especially that due to the F pairs in the acetone-d_6/2-propanol-d_8 system where satisfactory fits cannot be obtained if it is excluded. The results of these fits are given in Table 1 and Figures 1–3, which show the breakdown of the polarizations into the initial polarizations from the precursor and the geminate pairs and the subsequent thermal equilibration and F-pair polarizations developed in the separated radicals.

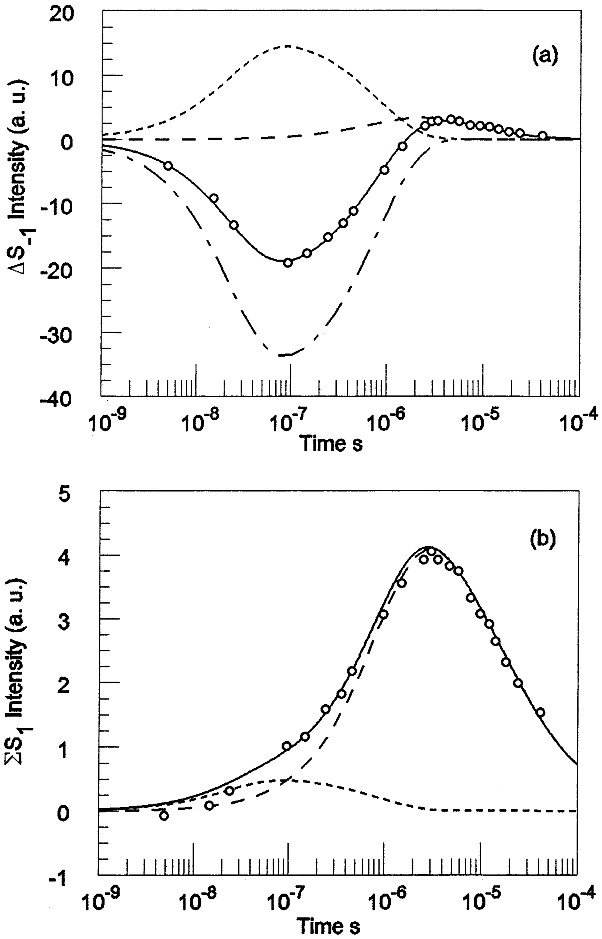

Figure 2. Least-squares fits to observed FT ESR spectra from the laser flash photolysis of 1 M acetone in triethylamine. (a) Difference of the amplitudes of the -1 and $+1$ hyperfine lines (ΔS_{-1}); $\Delta S_{-1} < 0$ and $\Delta S_{-1} > 0$ correspond to A/E and E/A polarizations, respectively. (b) Sum of the amplitudes of the -1 and $+1$ hyperfine lines (ΣS_1). In both cases the solid line (–) is the total least-squares fit, the small-dashed line (- - -) is from triplet reaction, the broken-dashed line (– - –) is from singlet reaction, the large-dashed line (— — —) is from separated radicals, and the experimental values (○) are from ref 10.

For acetone-d_6/2-propanol-d_8, the results for the rates of radical formation, bimolecular decay, and ST_0 polarizations are in reasonable agreement with Levstein and van Willigen,[9] but the present value for T_1 is approximately 3 times shorter than their result and is much closer to the experimental values of 2.7–4 μs found for the 2-propanolyl radical in 2-propanol.[9,12,22] As discussed in connection with eq 9, the difference may lie in the approximation to the integral in this equation for ΣS_M, as its use here over the entire time range gave $T_1 = 12$ μs vs their value of 9 μs and did not significantly worsen the fit to ΣS_M but made it impossible to fit satisfactorily the ΔS_M results. Several new results are obtained here. As already noted, spin exchange plays an important role, with the ratio $k_{ex}/(k_e p_S) = 1.8$ being typical of theoretical estimates.[21] The precursor reacts exclusively as a triplet, an expected result as the reaction of photoexcited acetone with 2-propanol is too slow (ca. 10^7 s^{-1}) to compete with singlet–triplet intersystem crossing.[23] The net radical polarization from the triplet, equal to $2\rho_T$ because the triplet yields two radicals, is $1.3\rho_{eq}$, confirming the original proposal by Paul,[3] and indications from quenching experiments,[13] that it is due to spin–lattice relaxation in the acetone triplet prior to reaction.

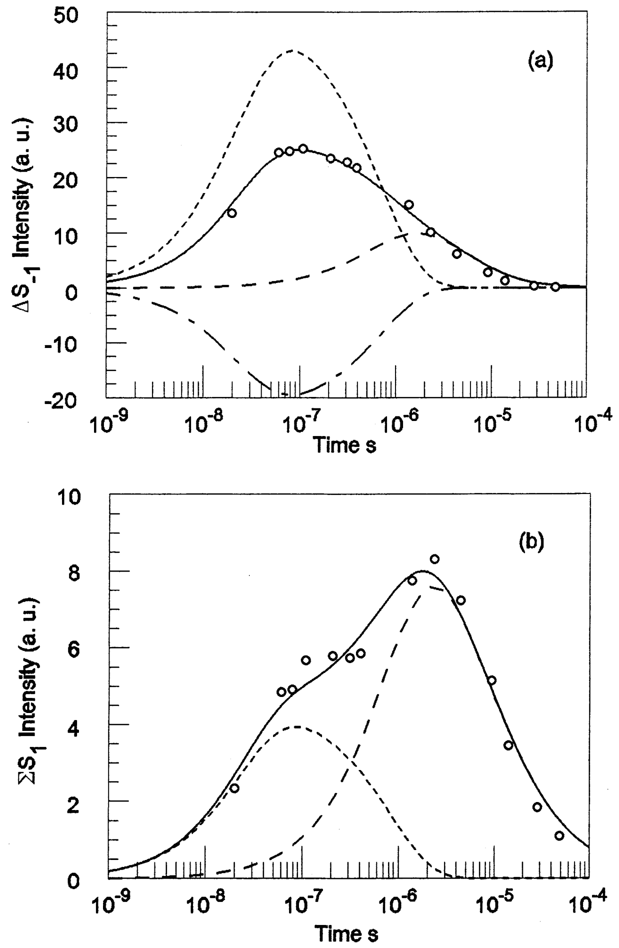

Figure 3. Least-squares fits to observed FT ESR spectra from the laser flash photolysis of 1 M acetone and 1 M triethylamine in benzene. (a) Difference of the amplitudes of the -1 and $+1$ hyperfine lines (ΔS_{-1}); $\Delta S_{-1} < 0$ and $\Delta S_{-1} > 0$ correspond to A/E and E/A polarizations, respectively. (b) Sum of the amplitudes of the -1 and $+1$ hyperfine lines (ΣS_1). In both cases the solid line (—) is the total least-squares fit, the small-dashed line (- - -) is from triplet reaction, the broken-dashed line (— - —) is from singlet reaction, the large-dashed line (— — —) is from separated radicals, and the experimental values (○) are from ref 10.

For the photolyses of acetone in triethylamine and in 1 M triethylamine in benzene, the values of the rates of radical formation, bimolecular recombination, and spin−lattice relaxation agree well with those of Ohara et al.[10] Spin exchange is definitely present but, as noted previously, less well-defined because of the very rapid spin−lattice relaxation in these systems. The reaction in neat triethylamine proceeds in roughly equal amounts by the singlet and triplet channels, indicating that the singlet reaction rate is comparable to the intersystem crossing rate. The apparent dominance of the singlet reaction, indicated by the observed initial A/E RPM polarization, is due to ST_0 RPM polarization being 3 times more efficient in a singlet radical pair than in a triplet where only the T_0 level is polarized. From the values of f_T as defined following eq 4, it is estimated that ${}^1k/k_{isc} = 0.79$ in a solution of 1 M acetone in triethylamine (this solution is approximately 6.7 M in triethylamine) and ${}^1k/k_{isc} = 0.16$ in a solution of 1 M acetone and 1 M triethylamine in benzene. The ratio of the ${}^1k$ rates in these two systems is in reasonable agreement with their triethylamine concentrations.

That the sizable triplet reaction component in the acetone/triethylamine photolysis contributes little to the net absorption ($2\rho_T = 0.20\rho_{eq}$) suggests that the triplet reacts before spin−lattice relaxation can occur and/or there is an emissive acetone TM polarization, as suggested by McLauchlan et al.[6] From the results for ρ_T in the acetone/triethylamine photolyses, one can extract estimates of ${}^3k/{}^3W$ and ρ_{TM}, using eq 6 and assuming that the values of ${}^3k$ for the two systems have the same ratio ($\cong$4.8:1) as their ${}^1k$ rates and that ${}^3W$ is approximately the same in triethylamine and benzene. This analysis gives ${}^3k/{}^3W \cong 8$ for the acetone/triethylamine system and $\rho_{TM}/\rho_{eq} \cong 0.03$; these results are not significantly affected by changes of 25% in the ratios of ${}^3k$ and ${}^3W$ in the two systems. These results indicate that the reaction of photoexcited acetone with triethylamine is considerably faster than the triplet spin−lattice relaxation rate, which is reasonable given that it is comparable to the singlet−triplet intersystem crossing rate and that the triplet mechanism is ineffective in triplet acetone.

Calculation of the ST_0 polarization[19,20] for a 2-propanolyl radical pair in 2-propanol at $T = 298$ K for which $D_{rel} = 2D = 1.1 \times 10^{-5}$ cm^2/s,[12] with the range parameter of the exchange interaction taken as $\lambda = 2.0 \times 10^8$ cm^{-1}, gave $\rho_{1,2,3}^{ST_0}/\rho_{eq} = 3.6$, 6.8, and 9.4 for the deuterated pair, in good agreement with the experimental values of Levstein and van Willigen,[9] and $\rho_1^{ST_0}/\rho_{eq} = 10.3$ for an ordinary protonated pair. Although this result appears to agree with the values extracted here for 2-propanolyl in triethylamine and benzene, it must be noted that the considerably lower viscosities of these solvents, at 25 °C $\eta = 0.347$ and 0.604 cP, respectively, vs 2.04 cP for 2-propanol,[24] are likely to increase the diffusion rate and thus reduce the ST_0 polarization. (The short spin−lattice relaxation times of 2-propanolyl in these solvents, which are undoubtedly due to the spin−rotation interaction as the hyperfine anisotropies of 2-propanolyl are too small to be effective, suggest this is the case. This mechanism gives $T_1 \propto \eta$,[25,26] thus predicting that the T_1 value in triethylamine and benzene should be one-fifth and one-third, respectively, of that in 2-propanol, in rough agreement with the observed values.) Estimating the diffusion rates in these solvents by multiplying the 2-propanol value by the ratio η(2-propanol)/η(solvent) gave a calculated $\rho_1^{ST_0}/\rho_{eq} = 4.8$ and 6.1 for a 2-propyl pair in triethylamine and benzene, respectively. Thus, this appears to be another example of observed values of $\rho_1^{ST_0}(H)/\rho_1^{ST_0}(D)$ for 2-propanolyl radicals being some 1.5−3 times greater than the calculated value of around 3.[3,9,27] This effect, which has been attributed to isotope effects on hydrogen bonding and other factors affecting diffusion in these solvents,[9] may account for the discrepancy between the observed and calculated values of the RPM polarization of 2-propanolyl in triethylamine and benzene.

In summary, fits to state-of-the-art FT ESR spectra of free radical reactions exhibiting CIDEP using model kinetic equations such as those developed here can provide extensive information about the mechanisms and dynamics of these reactions.

Appendix

To determine the effects of spin exchange, reaction, and RPM polarization during radical encounters, consider first a radical in state β,M encountering an α-spin radical at the reaction separation. If p_S is the probability of reaction in the singlet state, the pairs that survive and separate will be $\frac{1}{2}T_0$ and $\frac{1}{2}(1 - p_S)S$. The respective probabilities of the T_0 part separating as $R_{\beta M}R_\alpha$ and $R_{\alpha M}R_\beta$ are $\frac{1}{2}(1 - \rho_M^{ST_0})$ and $\frac{1}{2}(1 + \rho_M^{ST_0})$. The corresponding probabilities for the singlet part are obtained by reversing the sign of $\rho_M^{ST_0}$. Thus, the loss of β,M radicals and the gain of α,*M* radicals in this encounter are

$$\beta,M \text{ loss} = 1 - \frac{1}{4}(1 - \rho_M^{\mathrm{ST}_0}) - \frac{1}{4}(1 - p_\mathrm{S})(1 + \rho_M^{\mathrm{ST}_0}) = \frac{1}{2} + \frac{1}{4}p_\mathrm{S} + \frac{1}{4}p_\mathrm{S}\rho_M^{\mathrm{ST}_0} \quad \text{(A1)}$$

$$\alpha,M \text{ gain} = \frac{1}{4}(1 + \rho_M^{\mathrm{ST}_0}) + \frac{1}{4}(1 - p_\mathrm{S})(1 - \rho_M^{\mathrm{ST}_0}) = \frac{1}{2} - \frac{1}{4}p_\mathrm{S} + \frac{1}{4}p_\mathrm{S}\rho_M^{\mathrm{ST}_0} \quad \text{(A2)}$$

The corresponding loss of α,*M* radicals and gain of β,*M* radicals from a radical in state α,*M* encountering a β-spin radical are given by eqs A1 and A2, respectively, with the sign of $\rho_M^{\mathrm{ST}_0}$ reversed. Thus, the equation for the change in the population difference between the lower and upper electron spin levels of the *M*th nuclear spin state from this encounter is

$$\frac{\mathrm{d}S_M}{\mathrm{d}t} = -k_\mathrm{e}(N_{\beta,M}N_\alpha - N_{\alpha,M}N_\beta) - \frac{1}{2}k_\mathrm{e}p_\mathrm{S}\rho_M^{\mathrm{ST}_0}(N_{\beta,M}N_\alpha + N_{\alpha,M}N_\beta) \quad \text{(A3)}$$

Finally, noting that the first term on the right hand side of eq A3 describes the effects of spin exchange, we correct for the likelihood that this occurs at a larger separation than the reaction distance by replacing k_e in this term by k_ex to obtain eq 7 in the text.

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