Electron spin echo study of CIDEP in photolysis of di-t-butyl ketone at low temperatures

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ABSTRACT

Electron spin echo was used to study CIDEP of t-butyl radicals in toluene and 2-propanol. The cross-relaxation was found to be effective at low-temperatures and to have significant effect on the observed kinetics of CIDEP decay. Computer simulations allowed us to estimate the rates of cross-relaxation transitions and the magnitude of nuclear polarization.

INTRODUCTION

At short times, the radicals produced in a pulse very frequently show transient ESR spectra that differ significantly in magnitudes and phases from the equilibrium ones. This phenomenon is known as the chemically induced dynamic electron polarization (CIDEP) (ref.1) or, more generally, as the electron spin polarization (ESP), two main mechanisms accounting for the majority of its observations.

The first is triplet mechanism (TM) (ref.2). It operates on the fast reactions of the spin-polarized triplet molecules, some part of the triplets polarization is left in the escaping radicals. This results in emissive (E) or absorptive (A) ESR spectra with normal line intensity ratios, the sign being determined by the sign of zero field splitting value.

The second, known as the radical-pair mechanism (RPM), is responsible for the so-called multiplet CIDEP that is due to the singlet-triplet (ST) mixing in the geminate spin-correlated radical pairs (RP) or in the F-pairs formed by diffusing radicals. This mixing depends on the particular nuclear spin states of the radicals forming RP and thus makes ESP to be non-uniform across the spectrum. For RP,composed of radicals a and b, the polarizations are a function of quantity $Q_{ab} \propto (\omega_a - \omega_b)$, where ω_a, ω_b are the Larmor frequencies of the radicals in the given nuclear states m_a, m_b. The ST_0 mixing in both the triplet RP and F-pairs gives the E/A type of spectra with abnormal line intensity ratios, emissive low-field and absorptive high-field halves, for singlet RP one observes the opposite

A/E polarization. The ST_ mixing originates from radicals, forming a pair when they later on diffuse apart thus make S and T_ terms to cross for a moment. This results in slightly asymmetrical net emissive spectra with specific line intensity ratios and is observed noticeably for high viscosity.

It was recently found that TM and RPM are not responsible for all observed ESP patterns, and other phenomena were found such as polarization of biradicals (ref.3) and of RP itself (refs.4-6) show each line in spectrum to have EA polarization. The net emissive polarization mechanism was proposed (ref.7) and found in the quenching of duroquinone (ref.8), antraquinone (ref.9) and benzophenone triplets (ref.10) by stable radicals and also in quenching of the benzil and some other triplets by short-lived radicals (ref.11). On a longer time-scale other mechanisms are also found to determine ESP pattern (refs.30-31).

The main tool for the study of the ESP in a submicrosecond domain are based today on a broad band cw diode-detection technique known as the time-resolved ESR (TRESR) (ref.12). The pulsed in essence techniques, such as the electron spin echo (ESE) (ref.13) and Fourier transform ESR (refs.14,15) are also used and show their essential advantages.
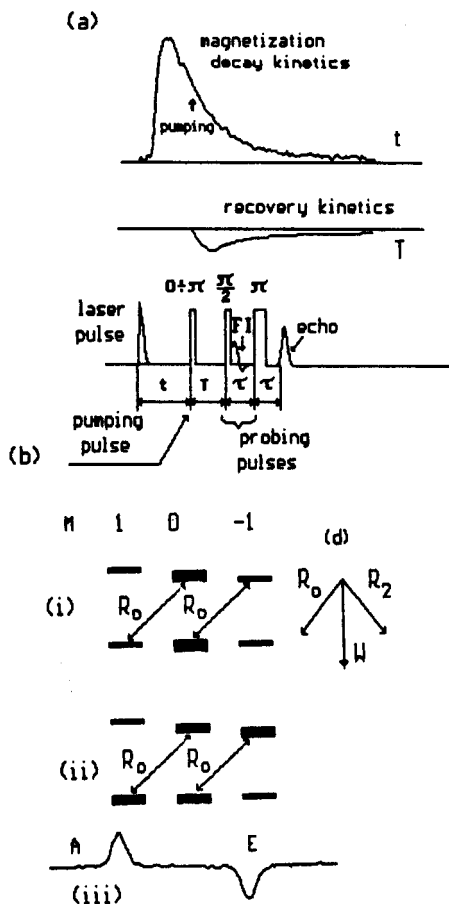

Fig.1:
The scheme of the ESE kinetic technique(a) and diagram illustrating convertion of CIDNP to ESP(b),filled rectangles reflects the populations of a radical with two equivalent nuclei with I=1/2 R_2 and R_0 correspond to the cross-relaxation transitions with changing of the summed electron and nuclear spin magnetic numbers to be equal $\Delta m=0$ and $\Delta m=2$, respectevely, W is responsible for the spin-lattice relaxation (d). The resulting A/E ESR spectrum is shown below (iii).

It was also realized that for certain conditions in some radicals, in particular, for those which have large hf constants, the cross-relaxation (CR) arising from modulation of the isotropic or anisotropic hf interactions by molecular motion might transform by spin sorting process CIDNP into ESP. This may cause invertion of the intial multiplet CIDEP from E/A in A/E on a longer time scale, provided nuclear polarization in radical is not small compared to CIDEP and CR is sufficiently fast (refs.16,17). For radicals with hf as large as 20 G both of these conditions may be well fulfiled. The mechanism of sign reversal is illustrated (Fig.1b) for the simplest case of the radical having two equivalent nuclei with I=1/2 and a positive hf constant. It is clear from the diagram how the R_0 transitions, governed by scalar CR mechanism, convert the initial CIDNP of EA type in radical (Fig.1-i) into A/E ESP (Fig 1-ii) (for triplet RP this E /A polarization means excess of the radicals with antiparallel α and β nuclear spins).

Using the TRESR techique, it was found that the invertion of the sign of multiplet CIDEP is sure to occure at least for the 2-propylketyl and t-butyl radicals but is visible at high radical concentrations (refs.18-20). The photolysis of acetone in 2-propanol for different temperatures has also been studied by ESE (ref.21) and time resolved NMR techniques (ref.22). The ESE studies show that at temperatures below 220K, the initial E/A polarization of 2-propylketyl radicals trasnsforms to the A/E at 10μs after the photolytic pulse. This behavior has been explained by the existence of a sufficiently high multiplet nuclear spin polarization in the radical which is transformed into electron spin multiplet polarization by means of CR due to scalar relaxation mechanism caused by rotation of methyl groups. Time-resolved NMR studies on the sign of multiplet effect in cage and escape products show both of them to be A/E contrary to the expected E/A for the bulk products as it follows from the Kaptein's rules. The NMR result seems to be in some disagreement with the ESR ones but may be referred to high magnetic field of NMR experiment.This discrepancy will not be discussed futher.

At room temperature in nonviscous solvents the CR rates are believed to be slow enough to provide marked influence on ESP. Thus, special conditions, for example, implying a sufficiently fast spin exchange to quench initial E/A polarization , should be found to obtain the ESP sign reversal (ref.19). By lowering the temperature and/or increasing viscosity the CR rates may be sufficiently increased and become comparable with spin-lattice relaxation rate W. So, as previously (ref.22), we have used the ESE technique to study the CIDEP of t-butyl radicals on the subject of the role of CR, especially, at low-temperatures.

In ESE, the magnetization of the radicals created by a photolytic pulse is detected *via* sequence of microwave pulses forming the spin-echo or free induction (FI) signals that gives a time profile of radical magnetization whose time behavior is determined by various sources. The

variety of reasons determine the ESP time evolution on a long time scale and so it is important to search for suitable methods to separate them. The possibility of changing CIDEP by influencing magnetization in a desired way is constructive and yet has been exploited in TRESR experiments to study electron exchange (ref.23) and also in ESE investigations on spin-lattice relaxation times of short-lived radicals (ref.24) and in ESE two-dimensional FT experiments on unstable radicals as well (ref.15).

EXPERIMENTAL

t-Butyl radicals were produced upon photolysis of the solutions, containing vol 1% of di-t-butyl ketone in toluene or 2-propanol, using a home-built XeCl laser running at repetition rate up to 4Hz. Solutions were circulating in a closed cycle gas-lift system, pure Ar being used both as carrier gas and oxygen remover. The quartz flow cell having inner dimensions of 3x3x15 mm was placed inside a quartz dewar tube mounted in a TE_{102} cavity of the ESE spectrometer (ref.25).

Temperature was monitored using a thermocouple placed into the cell 2 cm above the illuminated region and found to be stable in the limits of 0.5K. The lowest temperature achieved was 180K for 2-propanol and 150K for toluene. For solutions under study, lowering the temperature from ambient to the lowest attained with the given solution results in the decrease of the flowing rate from 2 to 0.1 ml/min due to the increase of the viscosity. Heating of the solution was measured not to exceed 1K in the worst case, i.e. the slowest flow, the maximum repetition rate and full photon flux up to 60 mW. To attenuate light pulse calibrated filter was placed in a light path.

A typical ESE experimental procedure (Fig.1a) implies the application of narrow mw pulses at different delays after the laser pulse with subsequent detection of the primary echo or FI signals to obtain magnetization time-profile of the desired spectral region. The ESE signal recorded in a field sweep mode gives the ESE induced ESR spectrum with a certain delay after radical creation.

There is another method which implies the application of the additional "pumping" microwave pulse to change magnetization of the choosen spectral region in a suitable manner. This pulse is set at a fixed delay t relative photolytic pulse and after a certain period of time T probing pulses are as usual used to detect the echo or FI signals.

The last procedure is used to discern the polarization sources operating on a longer timescale and already not buried under the large initial polarization. In its simpliest form, the method used may be referred to as "dynamic recovery tecnique" (ref.24). All other experimental details were the same as those described previously (ref.21).

RESULTS

In fig2(a) the ESE spectra of t-butyl radical in toluene for 190K and 230K are plotted for delay of 50 μs. It is clearly seen that for higher temperature the spectrum is indicative of the A^*/E polarization while for the lower temperature it obviosly shows E/A^*. This is in agreement with the previous studies (ref.19).

The central part of spectrum for the set of delays taken at 190K (Fig.2b) clearly shows that the spectrum shape undergoes marked distortion with time.
In fig.3 the time profiles are shown for the lines with
m=±1/2,±3/2 in common with the corresponding recovery curves for a 90° pumping pulse. The recovery kinetics for m=±5/2 are close to that for m=±3/2 and are not given in the figure.

The behavior of decay and recovery kinetics for the lines (note, ESE signals, we measured, reflects the magnetizations of the secondary splitted lines as a whole) that are symmetricaly positioned relative to centre of the spectrum looks rather similar , if to forget for a moment about the different levels they relax to. For the lines with m =±1/2 , the effect of sign reversal in recovery kinetics is less pronounced. Both of these features are expected from ESP due to CR determined by scalar relaxation.
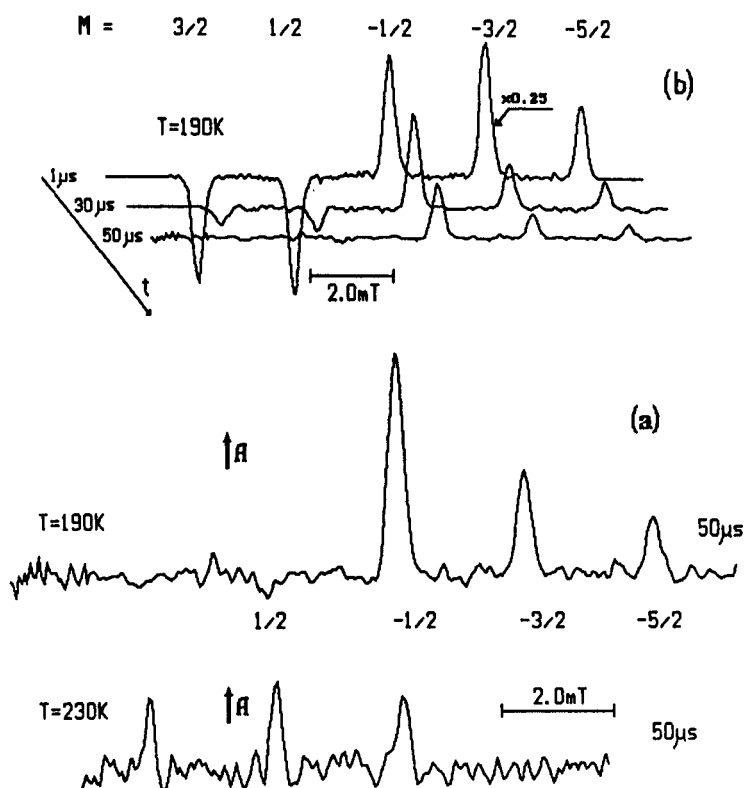

Fig.2: The central part of t-butyl radical spectrum recorded at different temperatures (a) and delays from laser pulse (b).
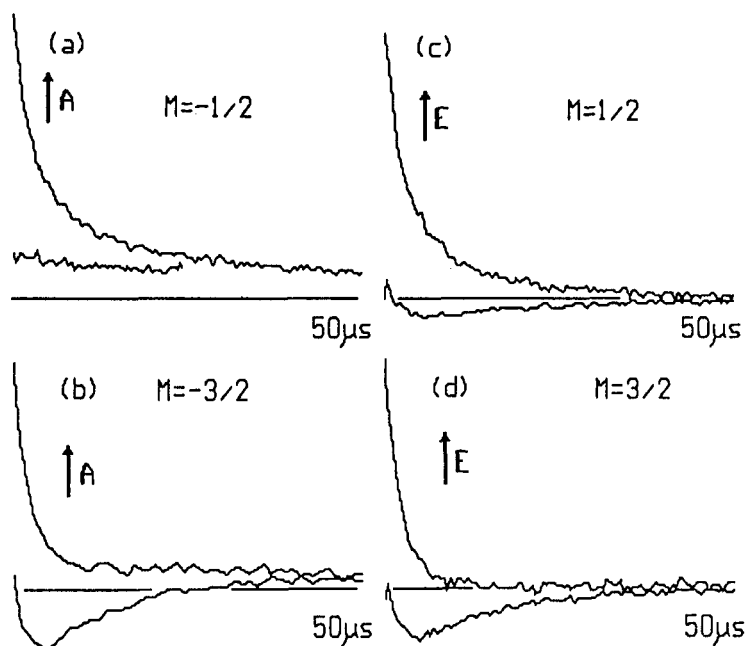
Fig.3: Time-profiles of the four centre lines of t-butyl radical
in toluene for 159K in common with corresponding recovery
kinetics.

For higher temperatures, the F-pair polarization overlaps and
prevents of the sign reversal in the recovery kinetics (Fig.4b). The
decrease in the light intensity makes the contribution of F-pairs to
diminish thus isolating the CR effect as (Fig.4a). This result points to
the fact that CR is very effective indeed at this temperature in t-butyl
radical so as for $(CH_3)_2\dot{C}OH$. Unfortunately, the F-pair polarization in
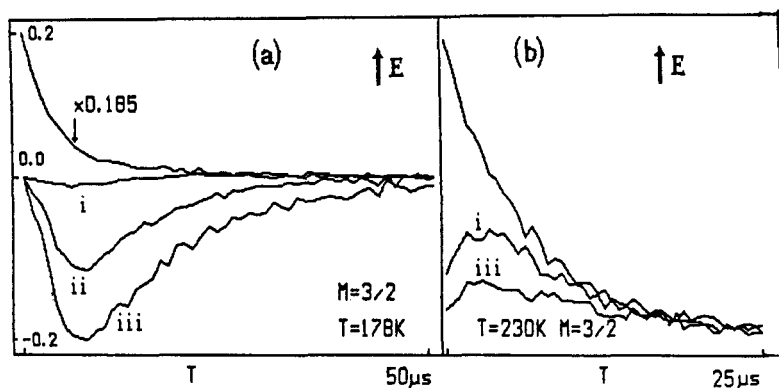

Fig.4: Recovery time-profiles of t-butyl radical in toluene
normalized to the initial unperturbed amplitude for
(a) 178K and (b) 230K, recorded for different levels
of light flux (i) - light unattenuated;
(ii),(iii) - attenuated to 60% and 36% respectively.

toluene is not low in experimental conditions and decays slowly for low temperatures thus overcoming A/E, created as believed on transfer of nuclear polarization, and preventing the sign reversal (Fig.3). Polarization transfer occurs within a shortened time interval and is masked by the large initial and F-pairs polarizations.
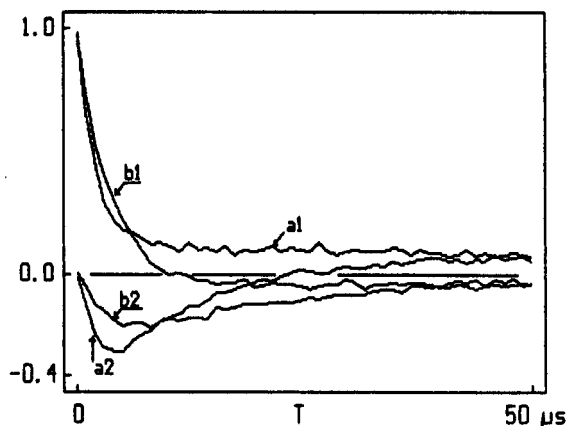

Fig.5: Time profiles of line with m=-3/2 of t-butyl radical in toluene at 156K (a1) and that for m=3/2 line of t-butyl radical in 2-propanol (inverted relative t-axis) at 182K (b1) both accompanied by corresponding recovery kinetics (a2,b2) obtained using 90° pumping pulse.

It is of interest to compare the results for the different solvents used. In Fig.5 the results for toluene and 2-propanol are presented for 156K and 182K, respectively. At these temperatures, the viscosities are believed to be close as follows from the similarity of the spectra (For toluene, the spectrum (Fig.6) may be reproduced satisfactorily if we suppose CIDEP enhancement to obey the dependence on Q of the type $Q^{0.5}-a \cdot Q$ (ref.32)). In 2-propanol, in contrast to toluene, the F-pairs seem to produce no considerable polarization at 182K and thus its E/A signal is overcomed by the nuclear polarization transfered *via* CR. From recovery kinetics CR in 2-propanol is visible to be some slower then in toluene thus being operative at the times where large initial polarization decays to a great extent.

Fig.6:
The spectrum of
t-butyl radical
in toluene at 155K

2.0mT

DISCUSSION

The shape of the central portion of the spectrum clearly indicates that except spin-lattice relaxation an extra mechanism exists on a longer timescale in a sufficiently wide temperature region. This mechanism manifests itself in changing of the spectrum shape at longer time scale (Fig.2) and also in substantially different time dependences for the intensities of lines with different m (Fig.3). The second is strongly confirmed by the recovery method. The recovery kinetics proved to be different for $m=\pm 1/2$ and $m=\pm 3/2$.

For estimating of the CR rates by computer simulations, we accept a simple model in which the spectral densities for fluctuating hf constants are the same for n equivalent nuclei with $I=1/2$ irrespectively on the summed nuclear spin, that results in two different CR rates R_0 and R_2, for transitions with Δm equal 0 and 2 respectively. For this model we may write the following set of equations for populations of radical energy levels

$$\dot{D}_m(t) = -(\frac{n}{2}k_d+2W)D_m - \frac{1}{2}k_s(a_{m+1}D_{m+1}+b_{m-1}D_{m-1})-$$

$$- \frac{1}{2}k_d(a_mS_m+a_{m+1}S_{m+1}-b_{m-1}S_{m-1}-b_mS_m)$$

$$\dot{S}_m(t) = -\frac{1}{2}k_s(a_mS_m-a_{m+1}S_{m+1}+b_mS_m-b_{m-1}S_{m-1})-$$

$$- \frac{1}{2}k_d(a_mD_m-a_{m+1}D_{m+1}-b_{m-1}D_{m-1}-b_mD_m)$$

$$a_m=n/2+m, \quad b_m=n/2-m, \quad K_s=R_0+R_2, \quad K_d=R_0-R_2 \qquad (1)$$

Here D_m, S_m are the differences and sums of populations of the upper and lower energy levels corresponding to the given nuclear spin magnetic number m. Initial ESP and nuclear populations were taken in form $D_m(0)=P_eE_m\varepsilon_{em}$, $S_m(0)=E_m(1-\alpha\varepsilon_{nm})$. Here E_m is the intensity of m-th line in equilibrium spectrum, P_e and α characterize the magnitude of polarization enhancement for the electron and nuclei respectively. Factors, responsible for the dependence on m of the polarization enhancement for electron and nuclear spins, are ε_{em} and ε_{nm} respectively. The first is calculated from the initial spectrum while the second for the pair. of t-butyl and acyl radicals is supposed to be proportional $|m|^{0.5}$ as follows from the existing theories for at least non high viscous solvents (refs.26-28). F-pairs are included in (1) in common with equilibrium spectrum as the constant addendum $F_m=E_m(1+ F\cdot\varepsilon_{em})$.

Calculations show that when one of the CR transitions is more effective than the other, the decay of transferred magnetization becomes much slower than in the case of comparable R_2 and R_0. Satisfactory fitting of the recovery curve (Fig.7) is acheived with the set of parameters
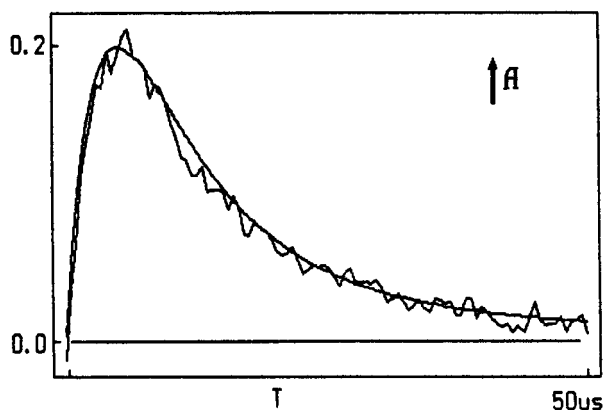
Fig.7:   Recovery of m=3/2 line of the t-butyl radical in
         toluene at 159K normalized to initial unperturbed
         decay kinetics and fitting to it using $R_o=0.015\mu s^{-1}$,
         $R_2=0.0075\mu s^{-1}$, $\alpha=0.1$, $P_e=20$, $F=0.6$, $W=0.067\mu s^{-1}$.

listed therein. Of course, these values are very approximate since first
we have three greatly unknown parameters α, R_o and R_2, and second the
distribution of nuclear populations ε_{nm} for the conditions of high
viscosity is not clear. But it may be not unexpected that CIDNP tends to
diminish at high viscosity. As has already been mentioned (ref.16) in the
case when nuclear polarization is less than a certain value (of the order
of electron polarization) the sign reversal could takes place in nuclear
rather than in electron spins manifold and CR manifests itself only in
slowing of electron polarization decay and making it to be nonexponential
and hyperfine dependent.

CONCLUSIONS

We found that the cross-relaxation becomes very efficient for t-butyl
radical at low temperature in toluene so as in 2-propanol. This is
contrary in some extent to TRESR results (ref.19) in sense of CR
polarization mechanism to be ineffictive for low temperatures. Even for
temperature as low as 159K the F-pairs contribute sufficiently in toluene
to prevent the sign reversal. This is not unexpected because the reported
recombination constant for t-butyl radicals is $9.8 \cdot 10^9$ mol^{-1} s^{-1} at 218K
(ref.29). It is also obvious that the observed kinetics (Fig.3 a-d) are
determined not only by the initial CIDNP transfer but also by the second
term in equations (1) which is responsible for the differential relaxation
of CIDEP itself. In what extent the above-mentioned mechanism influences
recovery kinetics could be determined from pulsed electron double
resonance experiment.

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