LETTERS TO THE EDITOR

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COMMUNICATIONS

Measurement of the rate of bimolecular electron spin relaxation between pairs of reactive radicals using time-resolved electron spin-echo spectroscopy[a)]

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The interaction between electron spins in pairs of reactive free radicals may produce the following effects on the EPR spectra of these species: (1) second-order decay of the signal by chemical reaction of the radicals,[1] (2) generation of chemically induced dynamic electron polarization (CIDEP),[2] and (3) spin relaxation induced by the electron exchange and dipole–dipole interactions. Although (1) and (2) have been studied extensively, (3) seems to have been so far reported only for stable radicals.[3]

We report here the use of time-resolved electron spin echo (ESE) spectroscopy to determine the radical–radical contribution to the spin-lattice relaxation time T_1 over a tenfold concentration range of the chemically reactive acetate radical $\cdot CH_2CO_2^-$, formed by pulsed 3 MeV electron radiolysis of basic solutions of potassium acetate saturated with N_2O.[4] The time dependences of the EPR signals of the low- and high-field lines of the $\cdot CH_2CO_2^-$ triplet were determined using a 90°-τ-180° spin echo sequence.[4] As shown in earlier work,[5–7] at very short times both lines are weakly absorptive,[6] increase in intensity under the influence of CIDEP, reach an extremum within a few microseconds, and gradually decay at longer times.

The time dependence of the magnetization M_λ of the λth hyperfine line is accounted for using Bloch-type equations[4] further modified to include strong Heisenberg exchange[8–11]:

$$[\dot{M}_{\lambda z} - \dot{M}^0_{\lambda z}] = -\omega_1 \mathrm{Im}\, M_{\lambda +} - \alpha_1(t)[M_{\lambda z} - M^0_{\lambda z}] - \nu_{ex}(t)\left[M^0_{\lambda z} - w_\lambda \sum M_{\lambda z}\right] + E_\lambda T_R(t)^{-1} M^0_{\lambda z}\,, \tag{1a}$$

$$[\dot{M}_{\lambda x} + i\dot{M}_{\lambda y}] \equiv \dot{M}_{\lambda +} = -i\omega_1 M_{\lambda z} - [\alpha_{2\lambda}(t) + i\Delta\omega_\lambda] M_{\lambda +} - w_\lambda \nu_{ex}(t)\left[M_{\lambda +} - \sum M_{\lambda +}\right]\,, \tag{1b}$$

where

$$\alpha_1(t) = T_{10}^{-1} + T_R(t)^{-1} + \nu_{ex}(t)\,;$$

$$\alpha_{2\lambda}(t) = T_{20}^{-1} + T_R(t)^{-1} + (1 - w_\lambda)\,\nu_{ex}(t)\,.$$

w_λ is the relative weight of the hyperfine line (e.g., $w_\lambda = \frac{1}{4}$ for the outermost lines of acetate radical) and T_{10} and T_{20} are concentration-independent relaxation times. For bimolecular decay of the initial radical concentration $R(0)$ with second-order rate constant $2k_d$,

$$T_R(t)^{-1} = (t + T_c)^{-1} = T_c^{-1} F(t) = 2k_d R(0) F(t)$$

and the decay of the hypothetical equilibrium magnetization $M^0_{\lambda z}$ is given by

$$\dot{M}^0_{\lambda z} = -T_R(t)^{-1} M^0_{\lambda z}\,.$$

Since electron exchange is also a second-order process we may write[12]

$$\nu_{ex}(t) = p T_R(t)^{-1} = 2k_{ex} R(0)\, F(t)\,.$$

The factor p is thus a measure of the ratio of cross sections for Heisenberg exchange and chemical reaction k_{ex}/k_d. A simple argument suggests that p should have a value close to unity: if electron dipole–dipole relaxation is negligible during an encounter, one-half of the radical pairs, i.e., those in which the electron spins are opposed, will lead to detectable exchange, but with only a 50% probability per encounter if exchange is strong.[8,13] It is likewise expected that only one-quarter of the encounters, those in the electronic singlet state, will lead to reaction.[14] It is the determination of p which constitutes the most important new result of this investigation.

The EPR signal in the ESE experiment described here is proportional to the value of $\mathrm{Im}\, M_{\lambda +}$ observed at the time $t + 2\tau$ following the *VdG* pulse. The initial longitudinal relaxation times including exchange $T_1(0)$

$$T_1(0)^{-1} = T_{10}^{-1} + p T_c^{-1}$$

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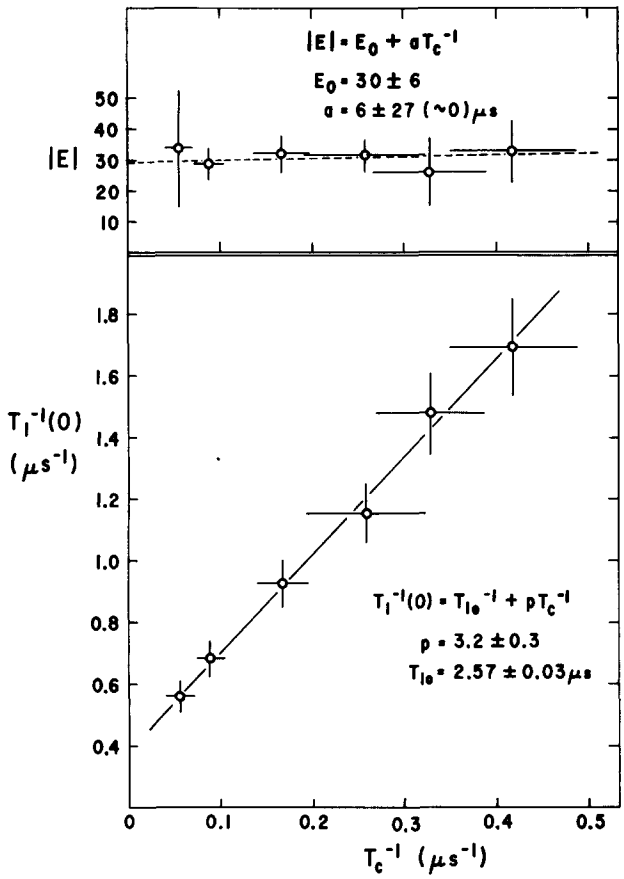

FIG. 1. Plots of enhancement factor $|E|$ (upper) and initial relaxation rates $T_1(0)^{-1}$ (lower) vs initial radical decay rate constant T_c^{-1}. Straight lines correspond to linear least squares fitting of data. Errors are one standard deviation.

were obtained for six different initial radical concentrations by iterative fitting of the time-resolved EPR signals from the outermost lines of $\cdot CH_2CO_2^-$ to Eq. (1) using T_c and the absolute value of the enhancement factor $|E|$ as additional adjustable parameters.[15]

The values of $T_1(0)^{-1}$ and $|E|$ for different values of T_c^{-1}, i.e., different initial radical concentrations, are summarized in Fig. 1. Two principal conclusions can be drawn from these results:

(1) The enhancement factor $|E|$ is independent of initial radical concentration up to the highest concentration achieved in this work ($\sim 4\times10^{-4}$ M, based on an estimated value of 1×10^9 for $2k_d$ for acetate radicals[16]). This is consistent with the assumption that CIDEP arises only from pair-wise interaction of radicals and that contributions from higher aggregates of radicals[17] or polarization quenching[17,18] are negligible. This is in accord with earlier measurements carried out at lower radical concentrations.[19]

(2) The cross section for bimolecular electron relaxation is substantially larger than that for radical–radical reaction ($p \simeq 3$). The fact that statistical factors alone are insufficient to predict p may be explained by postulating different steric constraints on electron exchange and chemical reaction in this case. The effect is also in the direction expected if the electron dipole–dipole interaction were contributing to electron exchange by mixing all four electron spin states of the radical pair.[8] The general procedure outlined in this communication is now being applied to the study of other reactive radicals.

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[1]A. D. Trifunac and R. G. Lawler, Magn. Reson. Rev. 7, 147 (1982).
[2]P. J. Hore, C. G. Joslin, and K. A. McLauchlan, Chem. Soc. Rev. 8, 29 (1979).
[3]R. N. Schwartz, L. L. Jones, and M. K. Bowen, J. Phys. Chem. 83, 3429 (1979), and references therein. A qualitative decrease in T_1 with increasing concentration for reactive radicals has recently been noted: R. W. Fessenden, J. P. Harnak, and B. Venkataraman, J. Chem. Phys. 74, 3694 (1981).
[4]A. D. Trifunac, J. R. Norris, and R. G. Lawler, J. Chem. Phys. 71, 4380 (1979).
[5]In the present apparatus the central line is obscured by a strong EPR signal from the quartz sample tube and could not be used in the analysis of the time-resolved spectra (Ref. 4).
[6]A. D. Trifunac, K. W. Johnson, B. E. Clifft, and R. H. Lowers, Chem. Phys. Lett. 35, 566 (1975).
[7]N. C. Verma and R. W. Fessenden, J. Chem. Phys. 65, 2139 (1976).
[8]M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, J. Chem. Phys. 51, 2690 (1969); G. J. Krüger, Advan. Mol. Relaxation Processes 3, 235 (1972).
[9]J. H. Freed, J. Phys. Chem. 71, 38 (1967); C. S. Johnson, Jr., Mol. Phys. 12, 25 (1967); J. H. Freed, J. Chem. Phys. 45, 3452 (1966).
[10]P. J. Hore and K. A. McLauchlan, Mol. Phys. 42, 533 (1981).
[11]P. J. Zandstra and S. I. Weissman, J. Chem. Phys. 35, 757 (1961); C. P. Cheng and S. I. Weissman, J. Phys. Chem. 80, 872 (1976).
[12]G. E. Pake and T. R. Tuttle, Jr., Phys. Rev. Lett. 3, 423 (1959).
[13]H. Shimizu, J. Chem. Phys. 42, 3599 (1965).
[14]M. Lehni, H. Schuh, and H. Fischer, Int. J. Chem. Kinet. 11, 705 (1979). See, however, R. M. Noyes, J. Am. Chem. Soc. 86, 4529 (1965).
[15]J. A. Syage, Ph.D. dissertation, Brown University, 1982; results to be published.
[16]P. Neta, M. Simic, and E. Hayon, J. Phys. Chem. 73, 4207 (1969).
[17]A. D. Trifunac, J. Am. Chem. Soc. 98, 5201 (1976).
[18]J. B. Pedersen, J. Chem. Phys. 59, 2656 (1973); J. H. Freed and J. B. Pedersen, Advan. Magn. Reson. 8, 1 (1976).
[19]R. W. Fessenden, J. Chem. Phys. 58, 2489 (1973).