

Figure 2. Calculated temperature dependence of $\langle Q^2 \rangle$ in the case of a Gaussian-barrier perturbed harmonic oscillator potential function: $\alpha h\nu_0$ represents the barrier height; ■, $h\nu_0 = 200 \text{ cm}^{-1}$; ×, $h\nu_0 = 400 \text{ cm}^{-1}$; ▲, $h\nu_0 = 130 \text{ cm}^{-1}$.

on the potential function chosen. As shown by Krusic et al.⁵ the temperature dependence of a_{13C} is negative provided that the barrier is high enough for a potential $V(Q) = -AQ^2 + bQ^4$ ($a > 0$; $b > 0$); on the contrary, the temperature dependence of a_{13C} is positive if the chosen potential is¹¹

$$V = h\nu_0[(Q^2/2) + \alpha \exp(-Q^2)]$$

as can be shown by using $\langle Q^2 \rangle$, calculated by Chan et al.¹¹ (see Figure 2).

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Reaction of Tri-*n*-butylstannyl with Oxygen. Electron Paramagnetic Resonance Evidence for a Pentacoordinate Stannylperoxy Radical^{1,2}

Sir:

It has been well established^{3,4} that trialkyl group 4b radicals, R_3M , where R is, for example, CH_3 and C_6H_5 and M is C, Si, Ge, Sn, and Pb, react rapidly with molecular oxygen to give the corresponding peroxy radicals $R_3MOO\cdot$. These radicals are characterized by high isotropic g factors, which in general

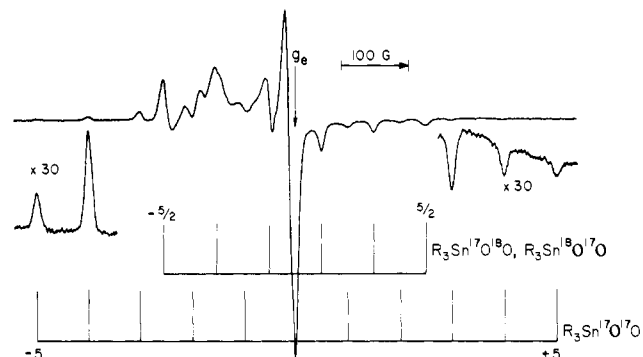


Figure 1. Anisotropic spectrum of $(n\text{-Bu})_3\text{SnOO}\cdot$ in cyclopropane at 93 K.

increase down the series $C < Si \sim Ge < Sn < Pb$, and exhibit no detectable central atom hyperfine splitting.

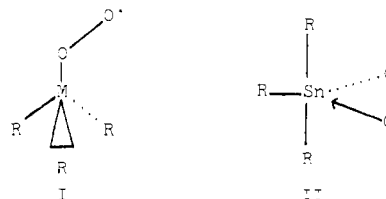
Alkylperoxy radicals enriched with oxygen-17 have an isotropic O hfsc of $\sim 23 \text{ G}$ from the terminal oxygen and an O hfsc of $\sim 18 \text{ G}$ from the penultimate oxygen.^{5,6} The ratio of spin densities on the two oxygens is approximately 2:1, in favor of the terminal oxygen.⁵ Trialkylsilylperoxy and trialkylgermylperoxy radicals also contain two inequivalent oxygen atoms with $a_{O'} \sim 25 \text{ G}$ and $a_{O''} \sim 15 \text{ G}$.⁷

The tri-*n*-butylstannyl radical, prepared by photolysis of a cyclopropane solution of di-*tert*-butyl peroxide and tri-*n*-butyltin hydride, reacted with oxygen enriched to 60% in oxygen-17 to give, at 213 K, an isotropic EPR spectrum consisting of an intense singlet ($g = 2.0265$) from a species with zero spin and one broad sextet, $a_O = 25 \text{ G}$, with an identical g factor from a species with one oxygen nucleus ($I = 5/2$) or from a species with two equivalent oxygen nuclei, e.g., $R_3\text{Sn}^{17}\text{OO}\cdot$ and $R_3\text{SnO}^{17}\text{O}\cdot$. Transitions from a doubly substituted species ($R_3\text{Sn}^{17}\text{O}^{17}\text{O}\cdot$) were not detected.

When a solution containing the radical was rapidly cooled to 93 K, an anisotropic spectrum was observed with $g_x = 2.0019$, $g_y = 2.0084$, $g_z = 2.0661$, in which a set of six equally spaced lines centered about g_x was resolved arising from the singly labeled species with $A_x(^{17}\text{O}) = 76.6 \text{ G}$ (Figure 1). In addition, 11 equally spaced satellites were observed from the species where both oxygen nuclei were labeled. No oxygen-17 hyperfine interaction could be observed about g_y or g_z but, by analogy with the alkylperoxy radicals, it would be expected to be $\sim 10 \text{ G}$.⁸ No further changes occurred in the spectrum on cooling to 4.2 K.

It is clear from the powder spectrum that the reaction of $(n\text{-Bu})_3\text{Sn}\cdot$ with O_2 gives an oxy radical with two magnetically equivalent oxygen atoms. The failure to observe the isotropic spectrum from $(n\text{-Bu})_3\text{Sn}^{17}\text{O}^{17}\text{O}\cdot$ must be associated with the inherently broad line widths of this species, since, in the alkylperoxy radicals, the line widths of the doubly labeled species are two- to four times greater than the singly labeled species.

We can, therefore, conclude from the results of this work that group 4b peroxy radicals down to germanium have the



usual peroxy radical structure I while the tri-*n*-butylstannylperoxy radical prefers a structure in which both oxygens are equivalently bound to the tin nucleus. A possible structure for the radical, consistent with these observations, is the pentacoordinate, trigonal bipyramidal structure II in which the vacant Sn 5d orbitals are used to form a dative bond with the

lone pair of electrons on the terminal oxygen atom. This structure, while unusual for a tin(IV) species, has been observed for several diamagnetic complexes such as $\text{Me}_3\text{SnCl}\cdot\text{C}_5\text{H}_5\text{N}$ and $\text{R}_3\text{Sn}(\text{oxinate})^9$ where a dative bond is formed through the lone pair on nitrogen.

Taking the principal values of the A tensor as (77,0,0) in the (x,y,z) axis system, the dipolar tensor gives a spin density of 0.5 in the $p\pi$ atomic orbital on oxygen, indicating that the electron is almost completely localized on the oxygen atoms. This is further substantiated by the absence of tin hyperfine from ^{117}Sn and ^{119}Sn .

A more detailed discussion of the chemistry of the trialkylstannylperoxy radicals, as well as other members of the group 4b peroxy radicals, will be presented in a future publication.

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CIDNP from Geminate Recombination of Radical-Ion Pairs in Polar Solvents

Sir:

When investigating the photoinduced electron transfer between donor (D) and acceptor (A) molecules with the chemically induced dynamic nuclear polarization (CIDNP)¹ technique, we have previously found² a correlation between the change of free enthalpy (ΔG) accompanying the reverse electron (back) transfer, the triplet energy (E_T) of A, and the phase of the CIDNP resonances (emission of absorption). The latter, according to the radical-pair theory of CIDNP,³ is correlated with a set of parameters characterizing the magnetic properties of the radicals, the spin multiplicity of the pairs, and the type of the reaction product monitored.⁴

The radical-pair theory of CIDNP assumes that geminate combination of radical pairs is spin selective and only possible for the singlet configuration. However, for pairs of radical ions ($\text{A}^{\cdot-} + \text{D}^{\cdot+}$) it has been shown⁵ that for $\Delta G > E_T(\text{A})$ triplet pairs also can undergo geminate recombination (to yield $^3\text{A} + \text{D}$). Singlet pairs can always recombine to yield $\text{A} + \text{D}$ in their ground states. Thus in systems where geminate recombination is not spin selective, D results from both singlet and triplet pairs, and intuitively no CIDNP is expected for D. The same would hold for $\Delta G < E_T(\text{A})$, if no other reaction pathway or spin randomization process except recombination existed to accommodate the nuclear spins with an alignment complementary to those which cause CIDNP in D.¹ However, CIDNP in D is observed in both cases, and it appears that separation of the pairs into individually solvated radical ions opens up an efficient (spin lattice) relaxation pathway for the nuclei, which, if the lifetime of the radical ions is sufficiently long, and thus randomizes the nuclear polarization in $[\text{D}^{\cdot+}]_s$, explains at least the CIDNP in the case of $\Delta G < E_T(\text{A})$.^{6,7}

To explain the CIDNP found in the case of $\Delta G > E_T(\text{A})$, we use an energy diagram similar to those proposed recently^{8,9} to explain the magnetic field dependence of the ^3A formation.

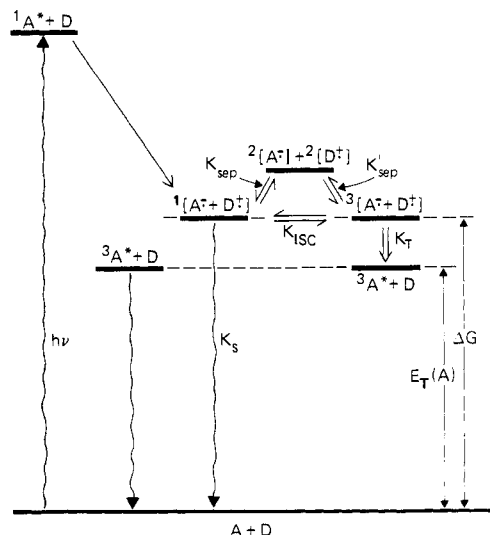


Figure 1. Energy Diagram for Radical-Ion Pair with $\Delta G > E_T(\text{A})$.

We assume that $E_T(\text{D}) > E_T(\text{A})$, and that D absorbs at shorter wavelengths than A. Let excitation of A yield the highly ionic exciplex $^1(\text{A}^-\text{D}^+)$, which in the polar solvents dissociates into radical-ion pairs $^1(\text{A}^{\cdot-} + \text{D}^{\cdot+})$. Hyperfine interaction and spin orbit coupling in the pairs has been shown^{8,9} to induce intersystem crossing (ISC), yielding pairs with triplet multiplicity $^3(\text{A}^{\cdot-} + \text{D}^{\cdot+})$. Now two possibilities have to be distinguished. (a) If $\Delta G < E_T(\text{A})$, only the singlet pairs can undergo geminate recombination; hence the spin selectivity is identical with that of neutral radical pairs, and the Kaptein Rule⁴ may be applied in the customary way to explain the CIDNP of D. (b) Figure 1 illustrates the case $\Delta G > E_T(\text{A})$. Now singlet pairs may recombine (k_{S}), undergo ISC (k_{ISC}), or separate into solvated radical ions (k_{sep}). Triplet pairs may recombine (k_{T}), undergo ISC (k'_{ISC}), or separate (k'_{sep}). Since $k_{\text{T}} \neq 0$, the above spin selectivity of the pair recombination does not apply. For $k_{\text{S}} = k_{\text{T}}$ and $k_{\text{sep}} = k'_{\text{sep}}$ the CIDNP enhancement should vanish, but according to our results it reaches a *maximum* for $\Delta G = E_T(\text{A})$.

We explain these findings as follows. The CIDNP phase and intensity of D depend upon the relative magnitude of the rate constants in Figure 1, especially on the ratio of $k_{\text{S}}/k_{\text{T}}$. We propose that the relative magnitude of k_{S} and k_{T} can be approximated using the energy gap law.^{10,11}

The energy gap law states that there is an inverse relation between the rates of radiationless transitions and the energy gap between the $v = 0$ levels of the states involved. Thus as long as a radiationless transition causes no significant change in geometry, the energy gap law states "The smaller the gap, the bigger the rate".¹¹

When applying the energy gap law to the system outlined in Figure 1, it follows readily that $k_{\text{S}} \ll k_{\text{T}}$, and consequently

$$\left. \begin{array}{l} \Delta G < E_T(\text{A}) \\ \Delta G > E_T(\text{A}) \end{array} \right\} \begin{array}{l} \text{the CIDNP in D stems} \\ \text{predominantly from} \end{array} \left\{ \begin{array}{l} \text{singlet pairs } (k_{\text{S}} \gg k_{\text{T}}) \\ \text{triplet pairs } (k_{\text{S}} \ll k_{\text{T}}) \end{array} \right.$$

Consider the example where A = naphthalene and D = triethylamine. This system with $E_T(\text{D}) > \Delta G > E_T(\text{A})$ was originally investigated by Taylor.¹² His unpublished results have been accidentally confused.⁷ We observed the methylene protons of D in enhanced absorption² and concluded, in agreement with Roth,¹³ that the CIDNP in D stems from triplet pairs. To explain the origin of the triplet pairs, we initially considered ISC in the exciplex.² However, more recent data clearly indicate that the triplet pairs stem from the originally formed singlet pairs via hyperfine and spin orbit coupling induced ISC, which is consistent with the results obtained recently by others¹⁴ who monitored the occurrence of ^3A in