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 $Me_3SnCl\cdot C_5H_5N$ and R_3Sn(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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Received July 15, 1977

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 found[2] 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 ($A^-\cdot + D^+\cdot$) it has been shown[5] that for $\Delta G > E_T(A)$ *triplet* pairs also can undergo geminate recombination (to yield $^3A + D$). Singlet pairs can always recombine to yield A + 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 $\Delta G < E_T(A)$, 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 $[D^+\cdot]_s$, explains at least the CIDNP in the case of $\Delta G < E_T(A)$.[6,7]

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

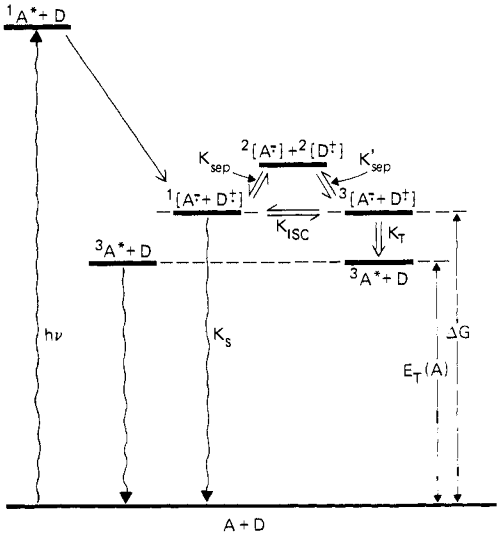

Figure 1. Energy Diagram for Radical-Ion Pair with $\Delta G > E_T(A)$.

We assume that $E_T(D) > E_T(A)$, and that D absorbs at shorter wavelengths than A. Let excitation of A yield the highly ionic exciplex $^1(A^-D^+)$, which in the polar solvents dissociates into radical-ion pairs $^1(A^-\cdot + D^+\cdot)$. Hyperfine interaction and spin orbit coupling in the pairs has been shown[8,9] to induce intersystem crossing (ISC), yielding pairs with triplet multiplicity $^3(A^-\cdot + D^+\cdot)$. Now two possibilities have to be distinguished. (a) If $\Delta G < E_T(A)$, only the singlet pairs can undergo geminate recombination; hence the spin selectivity is identical with that of neutral radical pairs, and the Kaptein Rule[4] may be applied in the customary way to explain the CIDNP of D. (b) Figure 1 illustrates the case $\Delta G > E_T(A)$. 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 $k_T \neq 0$, the above spin selectivity of the pair recombination does not apply. For $k_S = k_T$ and $k_{sep} = k_{sep}'$ the CIDNP enhancement should vanish, but according to our results it reaches a *maximum* for $\Delta G = E_T(A)$.

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_S/k_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 $k_S \ll k_T$, and consequently

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

Consider the example where A = naphthalene and D = triethylamine. This system with $E_T(D) > \Delta G > E_T(A)$ was originally investigated by Taylor.[12] His unpublished results have been accidentally confused.[7] We observed the methylene protons of D in enhanced absorption[2] 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 others[14] who monitored the occurrence of ^3A in similar systems with optical methods as a function of external magnetic fields. Our results provide independent evidence for the validity of this[14] explanation for the fast occurrence of ^{3}A, which has been a puzzle and the subject of controversy for some time.[15,16]

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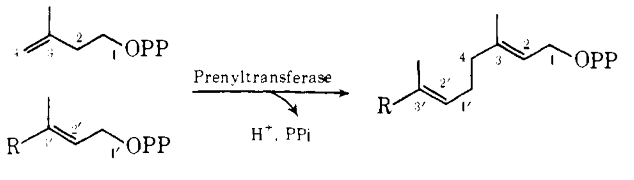
Received April 18, 1977

On the Mechanism of the Prenyltransferase Reaction. Metal Ion Dependent Solvolysis of an Allylic Pyrophosphate[1]

Sir:

The basic polymerization reaction of polyterpenoid biosynthesis is the condensation of C_4 of isopentenyl PP with the C'_1 of an allylic pyrophosphate with the concomitant elimination of pyrophosphate and the generation of the five-carbon homologue of the allylic substrate. This reaction is catalyzed by the enzyme prenyltransferase. Recently strong evidence has been presented that this reaction proceeds by an ionization–condensation–elimination mechanism.[2] The enzyme requires a divalent cation, Mg^{2+} or Mn^{2+}, for activity, and, since we have shown the substrates for prenyltransferase bind to the enzyme in the absence of these cations, we have concluded that these ions are required for catalysis rather than binding.[3] Thus, it is possible that the role of metal ions is to assist in ionization of the allylic substrate. This consideration, along with the indication that divalent cations enhance the solvolysis of allylic pyrophosphates,[4] has led us to undertake a more thorough examination of the solvolysis of allylic pyrophosphates in the presence of Mg^{2+} and Mn^{2+}. We have also measured metal ion dependent rates of solvolysis of chrysanthemyl PP which is an analogue of the immediate precursors of both squalene and phytoene.



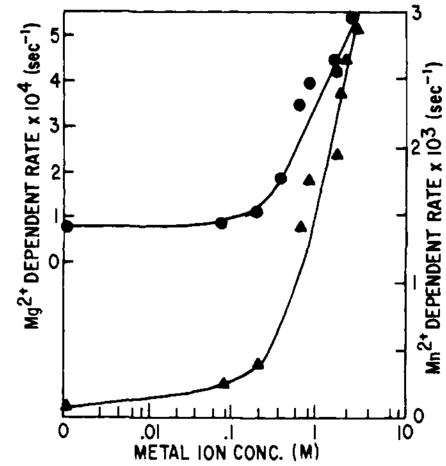


Figure 1. The effect of Mg^{2+} (●) and Mn^{2+} (▲) on the rate of solvolysis of geranyl PP. A constant ionic strength of 4.8 was maintained.[10]

Table I. Effect of Mg^{2+} on the Solvolysis of Chrysanthemyl Pyrophosphate

Mg^{2+}, M[a]	Rate × 10^4, s^{-1}
0	0.28
0.07	2.3
0.29	6.9
0.68	8.3
1.16	8.5
1.53	7.7

[a] A constant ionic strength of 4.8 was maintained.

For measuring rates of solvolysis, the pyrophosphates both labeled on the carbinol carbon with ^{3}H were sealed in ampules with 1 mL of buffered water containing variable concentrations of either $MgCl_2$ or $MnCl_2$ and NaCl to constant ionic strength.[5] After heating at 55 °C, the ampules were quenched at 0 °C and crushed, and the products of solvolysis extracted into hexane for radioisotope determination. First-order rates of solvolysis were obtained, each rate constant being determined by a set of six to nine time intervals. Rates were calculated from the slope of a least-squares plot of the data with the point of infinite solvolysis being set by acid hydrolysis of a control tube.

Alumina chromatography of the products indicated that 95% were alcohols and the remainder hydrocarbons. Analysis by GLC of the alcohols generated during solvolysis showed that geraniol and linalool were generated in a ratio of 1:5.[9] The proportions of the various products of solvolysis of geranyl PP were independent of the cation used. The products of solvolysis of chrysanthemyl PP were not analyzed.

The rates of solvolysis of geranyl PP at 55 °C as a function of Mn^{2+} and Mg^{2+} concentration are shown in Figure 1. The Mg^{2+}-dependent solvolysis rates of chrysanthemyl PP are in Table I. At metal ion concentration lower than 1 mM, the rates of solvolysis of geranyl PP were not significantly greater than that found in the absence of metal.[12] As the concentration of either divalent cation was increased from 1 to 10 mM, there was a gradual increase in the solvolysis of both substrates. Further increases in cation concentration from 0.07 M to ~1.5 M led to a large increase in the solvolytic rate. The limited solubility of NaCl prevented us from testing all divalent metal ion concentrations at the same ionic strength. The highest concentrations of Mg^{2+} were tested at an ionic strength of 12, and the rates observed were 1.8, 1.8, and 2.0 × 10^{-3} s^{-1} for 2.0, 2.3, and 2.63 M Mg^{2+}, respectively.[13] Thus, at these high