Table I. X-Ray Pattern Data[a]

KH	MgH_2	$KMgH_3$	$KMgF_3$[5]
3.30 (vs)	3.19 (vs)	4.003 (vw)	
2.86 (s)	2.76 (vw)	3.137 (vvw)	
2.02 (s)	2.495 (vs)	2.835 (vs)	2.80 (m)
1.72 (s)	2.29 (m)	2.311 (m)	2.29 (m)
1.43 (m)	1.59 (s)	2.007 (s)	1.99 (vs)
1.65 (m)	1.67 (s)	1.794 (vw)	
1.31 (m)	1.50 (m)	1.639 (s)	1.625 (m)
1.28 (m)	1.42 (w)	1.420 (m)	1.408 (m)
1.17 (m)	1.36 (w)	1.268 (m)	1.259 (w)
1.10 (m)	1.335 (w)	1.184 (m)	1.201 (s)
1.01 (w)	1.246 (w)	1.158 (w)	1.150 (w)
	1.150 (w)	1.122 (vw)	
	1.125 (w)		

[a] X-Ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46-cm diameter camera with Ni-filtered Cu Kα radiation. Line intensities were estimated visually.

does not cleave ether solvents. A preliminary study of the thermal properties of $KMgH_3$ as determined by simultaneous dta–tga analysis revealed a weak, broad, exothermic effect at ~250°, which may indicate disproportionation to KH and MgH_2, followed by endothermic effects at 300 and 380° due to decomposition of MgH_2 and KH, respectively. $KMgH_3$ was also prepared by a pyrolytic olefin elimination reaction when $KMg(sec\text{-}C_4H_9)_2H$ was heated in light mineral oil at 80° under vacuum.

$$KMg(sec\text{-}C_4H_9)_2H \xrightarrow{\Delta} KMgH_3 + 2C_4H_8 \quad (3)$$

Comparison of the powder pattern data for $KMgH_3$ with that of $KMgF_3$ suggests that these two compounds are isomorphous, a result predicted from the similar ionic radii of F^- and H^-. The Perovskite-like structure was demonstrated for $KMgF_3$[5] and is thus implied for $KMgH_3$. This structure is found for ABX_3 systems (A = B = metal cations, X = anion) in which one cation is much larger than the other. It is described as a cubic close-packed arrangement of the anions and the larger cations, with the smaller cations occupying octahedral positions in an ordered pattern.[6] It is proposed that each magnesium cation of $KMgH_3$ is surrounded by an octahedral arrangement of hydride ions. The crystal structure of MgH_2 was clearly shown[7] to be that of rutile, which also involves an octahedral array of hydride ions about each magnesium cation. The environment about magnesium in $KMgH_3$ and MgH_2 is therefore predicted to be essentially equivalent. Independent verification of this prediction is obtained from comparison of the infrared spectra (obtained as a Nujol mull between KBr salt plates) for these two compounds. MgH_2 exhibits two broad absorption envelopes centered at 1160 and 650 cm^{-1}. These are assigned to metal–hydrogen stretching and deformation vibrations, respectively. The infrared spectrum of $KMgH_3$ revealed two similarly broad absorptions centered at 1150 and 680 cm^{-1}. The absence of pronounced shifts is verification of nearly equivalent environments in these compounds.

We are currently investigating other routes to $KMgH_3$ and the preparation of related tri- and tetrahydridomagnesiate compounds. Detailed studies designed to describe the chemical and physical properties of these compounds are being carried out.

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(5) R. C. De Vries and R. Roy, *J. Amer. Chem. Soc.*, **75**, 2479 (1953).

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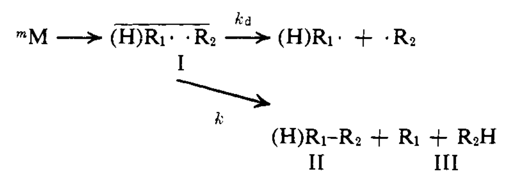
Theory of Chemically Induced Nuclear Spin Polarization. III.[1] Effect of Isotropic *g* Shifts in the Components of Radical Pairs with One Hyperfine Interaction[2]

Sir:

In two recent communications we have shown how hyperfine-coupling-induced singlet–triplet mixing in radical pairs can lead to large nuclear polarizations in products derived from radical coupling and disproportionation reactions.[1] Independently, Kaptein and Oosterhoff proposed a very similar mechanism and made the connection between nuclear and electron spin polarizations.[3,4] However, this model covers only part of the experimental observations and is restricted to radical pairs with at least two different protons coupled to the electrons in the radical pair. The polarization of the product is of the type in which the total nuclear Zeeman energy of the molecules is not changed from equilibrium (integral over entire spectrum = 0) and was termed entropy polarization.[5] In this communication, we wish to extend the theory and show that inclusion of spin–orbit coupling in the model can explain energy polarization in products (integral over polarized spectrum ≶ 0).

As a model, we consider a weakly coupled radical pair (I) generated from a precursor ^mM in a single step, where *m* denotes the multiplicity of M. A finite fraction of the radical pairs is assumed to react inside the solvent cage to give the combination or disproportionation products of II or III, with the remainder diffusing apart to give free radicals. For simplicity, it is assumed



$$^mM \longrightarrow \underset{\text{I}}{\overline{(H)R_1\cdot\ \cdot R_2}} \xrightarrow{k_d} (H)R_1\cdot + \cdot R_2 \qquad \searrow^{k}\ \underset{\text{II}}{(H)R_1\text{–}R_2} + R_1 + \underset{\text{III}}{R_2H} \quad (1)$$

that only one of the two components of I, [(H)$R_1\cdot$], has a proton spin strongly coupled to the electron spin

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(1) I and II of this series are: G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969).

(2) Supported in part by National Science Foundation (Grant GP-7043X) and the Petroleum Research Fund, administered by the American Chemical Society (Grant 3965-C4).

(3) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

(4) The two treatments differ in the formalism of the time dependence rather than in the underlying mechanism. In this and the following papers we adopt the Dutch authors' formalism which is based on the calculation of the time development of mixed states rather than the derivation of transition probabilities between pure states, although the results are necessarily the same.

(5) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **91**, 4549 (1969).

via a scalar hyperfine coupling of magnitude A. The spin Hamiltonian describing I in a magnetic field (H_0) can then be written

$$\mathcal{H} = \mathcal{H}_{\mathrm{EZ}} + \mathcal{H}_{\mathrm{NZ}} + \mathcal{H}_{S \cdot S} + \mathcal{H}_{I \cdot S} + \mathcal{H}_{S \cdot L} + \mathcal{H}_{\mathrm{D}} \quad (2)$$

where the first two parts are the electron and nuclear Zeeman energies; the third and fourth parts describe the scalar electron exchange and scalar hyperfine couplings; and the last two terms represent spin–orbit coupling and all dipolar interactions, respectively. We eliminate $\mathcal{H}_{\mathrm{NZ}}$ as unimportant and neglect $\mathcal{H}_{\mathrm{D}}$.[6] Furthermore, recognizing that $\mathcal{H}_{S \cdot L}$, in a freely tumbling radical in solution, shifts the g factor from the value of the free electron, we can combine $\mathcal{H}_{\mathrm{EZ}}$ and $\mathcal{H}_{L \cdot S}$ by introducing g_1 and g_2 as the isotropic g factors of components 1 and 2 of I, respectively.[7] Expressing all energies in angular frequency units, we write the Hamiltonian as

$$\mathcal{H} = \beta H_0(g_1 S_1 + g_2 S_2) - J(1/2 + 2S_1 \cdot S_2) + AI \cdot S_1 \quad (3)$$

where β is the Bohr magneton, S_1, S_2, and I are the electron and nuclear spin operators, and J is the scalar electron exchange coupling constant.[8] For small values of J we write the wave function of I as a mixture of the unperturbed electron singlet function, $S = 2^{-1/2}(\alpha\beta - \beta\alpha)$, and the triplet component, $T_0 = 2^{-1/2}(\alpha\beta + \beta\alpha)$. Mixing with $|1,1\rangle$ and $|1,\bar{1}\rangle$ is considered unimportant because of the large energy gap.[1,3] Using the method of variation of constants to describe the time dependence we obtain eq 4, the wave function for the two nuclear spin states, α_{N} and β_{N}. From the

$$\begin{aligned} \Psi^+(t) &= [C_S{}^+(t)S + C_{T_0}{}^+(t)T_0]\alpha_{\mathrm{N}} \\ \Psi^-(t) &= [C_S{}^-(t)S + C_{T_0}{}^-(t)T_0]\beta_{\mathrm{N}} \end{aligned} \quad (4)$$

time-dependent Schrodinger equation and (3), we get

$$i\frac{\partial C_S{}^\pm}{\partial t} = C_S{}^\pm J + C_{T_0}{}^\pm(1/2\beta H_0 \Delta g \pm 1/4 A) \quad (5)$$

$$i\frac{\partial C_{T_0}{}^\pm}{\partial t} = C_S{}^\pm(1/2\beta H_0 \Delta g \pm 1/4 A) - C_{T_0}{}^\pm J \quad (6)$$

where $\Delta g = g_1 - g_2$.

Integration depends on the state of I at the instant of its formation ($t = 0$). If we consider the case of a triplet precursor ($m = 3$), then $C_{T_0}{}^\pm(0) = 1$ and $C_S{}^\pm(0) = 0$.

$$C_S(t)^\pm = -i\frac{1/2\beta H_0 \Delta g \pm 1/4 A}{D^\pm} \sin D^\pm t$$

$$C_{T_0}{}^\pm(t) = \cos D^\pm t - i\frac{J}{D^\pm} \sin D^\pm t$$

where

$$D^\pm = [(1/2\beta H_0 \Delta g \pm 1/4 A)^2 + J^2]^{1/2}$$

Since product formation should depend on the degree of singlet character in I it should be proportional to eq 7. Examination of (7) shows that products with different nuclear spin states will be formed with different rates, attributable to the dependence of the mixing coefficient on the nuclear spin state, $1/2\beta H_0 \Delta g + 1/4 A$ for α_{N} and $1/2\beta H_0 \Delta g - 1/4 A$ for β_{N}. It also shows that if $\Delta g = 0$ both spin states build up in the product with equal rates giving no polarization. The sign of the polarization depends on the relative signs of A and Δg and, therefore, the same mechanism can account for both signal enhancement and emission. As pointed out before,[1,3] the magnitude of the polarization depends also on the mean lifetime of I. Averaging over the lifetime, τ, gives the rates of population increase of the two nuclear spin states (w^+ for α_{N} and w^- for β_{N}) in the cage product (eq 8) where k_{SE} is the specific rate

$$[C_S{}^\pm(t)]^2 = \frac{(1/2\beta H_0 \Delta g \pm 1/4 A)^2}{D^{\pm 2}} \sin^2 D^\pm t \quad (7)$$

$$w^\pm = k_{\mathrm{SE}}\frac{2(1/2\beta H_0 \Delta g \pm 1/4 A)^2 \tau^2}{1 + 4D^{\pm 2}\tau^2} \quad (8)$$

constant for cage product formation from the pure singlet state of the radical pair. If I is derived from a singlet precursor ($m = 1$), product formation should be proportional to eq 9, which leads to the opposite

$$w^\pm = k_{\mathrm{SE}}\left[1 - \frac{2(1/2\beta H_0 \Delta g \pm 1/4 A)^2 \tau^2}{1 + 4D^{\pm 2}\tau^2}\right] \quad (9)$$

polarization as observed from a triplet precursor.

We believe that this mechanism is superior to the Fischer mechanism, which is based on cross-relaxations in free radicals,[9] because (i) it allows both entropy and energy polarization to be explained by the same phenomenon, namely singlet–triplet mixing in radical pairs by hyperfine interaction and different g shifts in the components of the radical pair; (ii) it provides for different and predictable signs of polarization with no need for different interaction mechanisms between electron and nuclear spin; (iii) it puts no Overhauser limit on the magnitude of the polarization (assuming for a hypothetical reaction proceeding *via* a triplet precursor with $\Delta g = 10^{-3}$, $A = 2.5 \times 10^8$, $J \sim 10^8$ radians/sec, $\tau = 10^{-9}$ sec, and 98% product formation *via* nuclear spin state independent mechanisms, one obtains an enhancement factor of 4×10^3 at an nmr observation frequency of 60 MHz at 300°K); (iv) the polarization should be a function of H_0;[10] (v) this mechanism puts no limit on the lifetime of the *free* radicals because polarization occurs only in radical pairs.

The accompanying communications describe experimental results which are readily explained by this mechanism but are difficult to understand with the previous model.

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(6) The justification for this simplification will be presented in a future publication.

(7) The g shift arises from an interplay of spin–orbit ($S \cdot L$) and orbit–Zeeman interaction ($H \cdot L$). *Cf.* C. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., 1963, p 179.

(8) The exchange coupling is written here in different form from that used in ref 1 and differs from the previous treatment by a factor of -2. We have adopted this form to achieve uniformity with that used in ref 3.

(9) H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and references therein.

(10) *Cf.* M. Lehnig and H. Fischer, *Z. Naturforsch.*, in press; H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *J. Amer. Chem. Soc.*, **91**, 4929 (1969). Our model is not valid at very low field because it neglects mixing with $|1,1\rangle$ and $|1,\bar{1}\rangle$ which becomes important in the low field region.