Theory of Chemically Induced Nuclear Spin Polarization. IV. Spectra of Radical Coupling Products Derived from Photoexcited Ketones and Aldehydes[1]

Sir:

In the preceding communication we have examined the effect of hyperfine coupling and g shifts on singlet–triplet mixing in radical pairs with one coupled nuclear spin.[2] We now wish to extend this model to include many nuclear spins and to present experimental evidence in support of the theory. A simple extension of the previous considerations shows that the rate of population increase in the product with nuclear spin state j in a radical cage combination reaction with a triplet precursor is given by eq 1. The triplet–singlet mixing coefficients, M_j, for n nuclear spins take the form

$$w_j = k_{\mathrm{SE}}\frac{2M_j{}^2\tau^2}{1 + 4(M_j{}^2 + J^2)\tau^2} \tag{1}$$

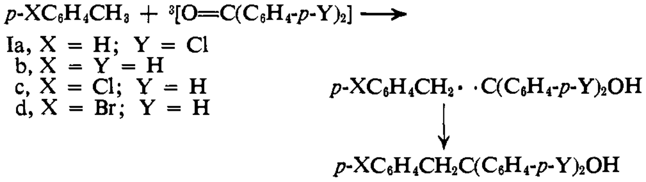
$$M_j = \beta H_0\Delta g/2 + \sum_{i=1}^{n}\epsilon_{ij}A_i/4$$

with $\epsilon_{ij} = +1$ or -1. The enhancement factor of an nmr transition between states j and k is given by eq 2,

$$P_{jk} = \frac{\langle I_{jk}\rangle - \langle I_{jk}\rangle_0}{\langle I_{jk}\rangle_0} \simeq \frac{\langle I_{jk}\rangle}{\langle I_{jk}\rangle_0} = \frac{w_k - w_j}{(w_k + w_j + 2w_{\mathrm{er}})\langle I_{jk}\rangle_0} \tag{2}$$

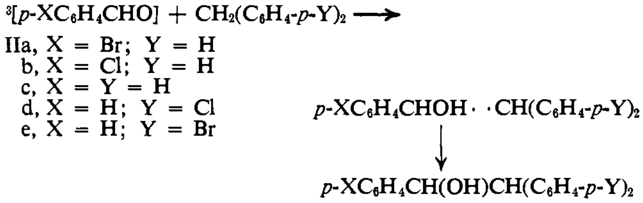
where $\langle I_{jk}\rangle$ and $\langle I_{jk}\rangle_0$ are the expectation values of the nuclear spin in the polarized product and at thermoequilibrium, respectively, and $k_{\mathrm{SE}}w_{\mathrm{er}}$ is defined as the rate of population of states j and k by all nuclear spin independent mechanisms.

The photochemical radical combination reactions I and II provide examples to test the theory. The reactions of the triplet states of benzophenones with



$$p\text{-}\mathrm{XC_6H_4CH_3} + {}^3[\mathrm{O{=}C(C_6H_4\text{-}}p\text{-}\mathrm{Y)_2}] \longrightarrow p\text{-}\mathrm{XC_6H_4CH_2\cdot\ \cdot C(C_6H_4\text{-}}p\text{-}\mathrm{Y)_2OH} \longrightarrow p\text{-}\mathrm{XC_6H_4CH_2C(C_6H_4\text{-}}p\text{-}\mathrm{Y)_2OH}$$

Ia, X = H; Y = Cl
b, X = Y = H
c, X = Cl; Y = H
d, X = Br; Y = H



$${}^3[p\text{-}\mathrm{XC_6H_4CHO}] + \mathrm{CH_2(C_6H_4\text{-}}p\text{-}\mathrm{Y)_2} \longrightarrow p\text{-}\mathrm{XC_6H_4CHOH\cdot\ \cdot CH(C_6H_4\text{-}}p\text{-}\mathrm{Y)_2} \longrightarrow p\text{-}\mathrm{XC_6H_4CH(OH)CH(C_6H_4\text{-}}p\text{-}\mathrm{Y)_2}$$

IIa, X = Br; Y = H
b, X = Cl; Y = H
c, X = Y = H
d, X = H; Y = Cl
e, X = H; Y = Br

toluenes (I) are examples of systems with two identical protons coupled to component 1 of the radical pair (the OH proton is rapidly exchanged in the product and does not count).[3] The mixing coefficients for this system are given in the first column of Table I. Since all nmr transitions are degenerate, no polarizations should be observed for $\Delta g = 0$. Since g is related to the spin-orbit coupling parameter λ, which increases with atomic number of the substituent atoms, Δg should increase from Ia to Id and should be negative for Ia, b and positive for Ic, d.[4] With $A_1 = A_2 < 0$ this predicts absorption lines for the methylene protons in reactions Ia, b while emission should be observed for Ic, d. Figure 1 shows the observed spectra which are in agreement with these predictions.

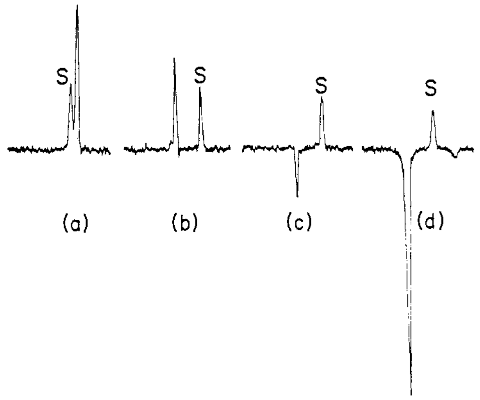


Figure 1. Spectra of the benzylic methylene protons in reactions Ia–d. S denotes the low-field ^{13}C satellite of the solvent (p-$\mathrm{XC_6H_4CH_3}$) methyl group. Field increases from left to right.

Table I. Mixing Coefficients, M_j, for Systems with Two Nuclear Spins

j	Both spins on component 1 M_j	One spin on each component[a] M_j
$\beta\beta$	$\beta H_0\Delta g/2 - A_1/4 - A_2/4$	$\beta H_0\Delta g/2 - A_1/4 + A_2/4$
$\alpha\beta$	$\beta H_0\Delta g/2 + A_1/4 - A_2/4$	$\beta H_0\Delta g/2 + A_1/4 + A_2/4$
$\beta\alpha$	$\beta H_0\Delta g/2 - A_1/4 + A_2/4$	$\beta H_0\Delta g/2 - A_1/4 - A_2/4$
$\alpha\alpha$	$\beta H_0\Delta g/2 + A_1/4 + A_2/4$	$\beta H_0\Delta g/2 + A_1/4 - A_2/4$

[a] Nuclear spin characterized by A_1 is on component 1; $\Delta g = g_1 - g_2$.

In the reactions of the photoexcited states of benzaldehydes with diphenylmethanes (II) the two nuclear spins are on different components of the radical pairs and all four nmr transitions are observable. The mixing coefficients for this system are given in the second column of Table I with the hydroxybenzyl radical defined as component 1. Substituent effects in this system predict decreasing Δg from IIa to IIe, with the first three reactions characterized by positive values. The spectra are given in Figure 2. Using reported hyperfine coupling constants for the hydroxybenzyl and benzhydryl radicals of -2.8 and -2.1 10^8 radians/sec[5] and assuming $J = 10^8$ radians/sec, $\tau = 10^{-9}$ sec, and $w_{\mathrm{er}} > 50w_j$, Δg has been adjusted to reproduce the relative intensities of the four transitions. The calculated spectra shown in Figure 2 are based on Δg values for reactions IIa–IIe of 2.7×10^{-3}, 1.5×10^{-3},

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

[2] G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92,** 2183 (1970).

[3] Reaction Ib was previously reported but had been interpreted by the cross-relaxation mechanism: G. L. Closs and L. E. Closs, *ibid.*, **91,** 4550 (1969).

[4] J. Sinclair and D. Kivelson, *ibid.*, **90,** 5074 (1968), give an approximation of the displacement of g from the free-electron value as $\delta g = {}^2/_3\Sigma(\lambda_i\rho_i/\Delta E_i)$ with ρ_i as the spin density on the substituted heavy atom and ΔE_i the energy gap between ground and excited states. This leads to positive δg for heavy atoms at the *ortho, para,* and benzyl positions.

[5] H. Fischer, *Z. Naturforsch.*, 20, 488 (1965); N. M. Atherton and R. S. F. Harding, *J. Chem. Soc.*, 5587 (1964).

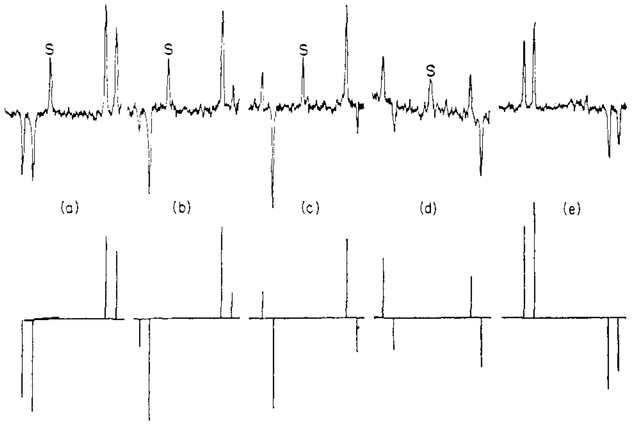

Figure 2. Experimental and calculated spectra of the benzylic protons in reactions IIa–e. Field increases from left to right. The low-field doublet originates from the proton on the hydroxybenzyl carbon atom. S denotes the low-field ^{13}C satellite of the methylene protons of the solvent [$CH_2(C_6H_4$-p-$Y)_2$].

0.47×10^{-3}, -0.33×10^{-3}, and -2.7×10^{-3}, respectively. The calculated spectra should be taken as demonstrative rather than as a best fit to the experimental data because the assumed invariance of the hyperfine coupling constants with introduction of substituents cannot be expected to hold strictly.[6] Nevertheless, the calculated g shifts are within expectations, and the general reproduction of the experimental results constitutes a strong support for the theory.

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[6] For an exact solution, the phenyl protons would have to be included in the model. The relative intensities do not vary very much with J and w_{er}, which affect mostly the absolute intensities.

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Theory of Chemically Induced Nuclear Spin Polarization. V. Comparison of Coupling Reactions in Singlet and Triplet Derived Radical Pairs and of Radicals Not Generated in Pairs[1]

Sir:

In a series of recent communications we have shown that singlet–triplet mixing *via* hyperfine interaction and g shifts in radical pairs provides a suitable model for explaining chemically induced nuclear spin polarizations.[2–4] The theory has been tested with several photochemical coupling reactions in which the coupling radicals were generated in pairs and had triplet precursors. In this communication, we wish to show that the theory is equally capable of accounting for spectra of products obtained from radical pairs (RP) with singlet precursors, as well as coupling products of radicals not generated in pairs. As examples we have studied the formation of 1,1,2-triarylethanes (E) from benzhydryl and benzyl radicals *via* three different reaction paths: the photochemical formation of triplet diphenylmethylenes followed by hydrogen abstraction from toluenes (I),[5] the thermolyses of the corresponding azo compounds (II),[2b] and the formation of benzyl and benzhydryl radicals from mixtures of diphenylmethanes and toluenes *via* hydrogen abstraction with benzoyl peroxide (III).

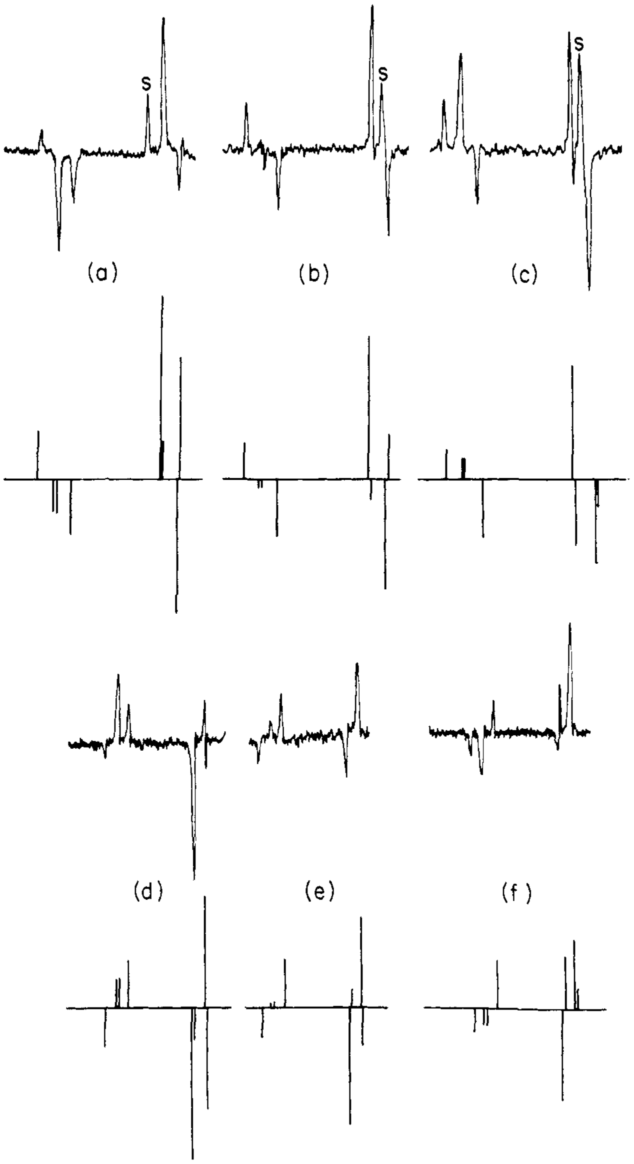

Figure 1. Experimental and calculated spectra of the benzylic protons in E formed in reactions Ia–c and IId–f. Field increases from left to right with the low-field multiplets originating from the methine protons. S denotes ^{13}C satellites of CH_3 groups in $CH_3C_6H_4$-p-Y solvents.

The singlet–triplet mixing coefficients in RP for the eight nuclear spin states of the benzylic protons (AB_2 system) are listed in Table I. From these and eq 1 and 2 of ref 4, the polarizations of the individual transitions in E derived by reactions Ia–c can be calculated with the spin Hamiltonian and kinetic parameters. Figure 1 (spectra a–c) shows the experimental results with the calculated relative intensities of the transitions based on the following parameters: $A_1 = -2.1 \times 10^8$, $A_2 = -2.9 \times 10^8$,[6] $J = 10^8$ radians/sec, $\tau = 10^{-9}$ sec, and

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

[2] (a) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969).

[3] G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970).

[4] G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970).

[5] G. L. Closs and L. E. Closs, *ibid.*, **91**, 4549 (1969).

[6] N. M. Atherton and R. S. F. Harding, *J. Chem. Soc.*, 5587 (1964); H. Fischer, *Z. Naturforsch.*, **20**, 488 (1965).