# Effect of Localized Unsaturation on the Scalar Exchange Coupling in Flexible Biradicals

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Received: September 29, 1992; In Final Form: December 20, 1992

Time-resolved electron paramagnetic resonance (TREPR) spectra of flexible biradicals containing one and two double bonds are reported. Simulation of the strongly spin-polarized spectra allows determination of the scalar electronic exchange coupling J and the encounter rate  $k_{en}$  between the two radical centers. Comparison of each unsaturated biradical with the saturated analogue of similar chain length shows that the J coupling increases with the double bonds present. This and other effects, such as that of the solvent on saturated biradical EPR spectra, are modeled and discussed in terms of both through-bond (TB) and through-solvent (TS) coupling mechanisms. Monte Carlo simulations of the chain dynamics and semiempirical molecular orbital calculations of overlap integrals support the hypothesis that isolated trans double bonds decrease the TS component of the J coupling while increasing the TB component.

## Introduction

Exchange couplings in biradicals are a subject of continued interest, particularly with regard to the mechanism of the interaction, i.e., through-bond, through-space, or through-solvent.1 Several studies of flexible biradicals in solution have suggested that all of these mechanisms can be important and that they are strongly dependent on temperature.<sup>2</sup> Recent advances in spectroscopic methods have made it possible to study such couplings in detail,<sup>3</sup> in particular by time-resolved magnetic resonance techniques.<sup>4</sup> Both magnetic parameters (spin-spin couplings) and kinetic parameters (chemical reaction, spin relaxation, and end-to-end encounter rates) have been determined with a high degree of accuracy for structurally simple biradicals such as saturated polymethylene chains.<sup>5</sup> Recently, we have put forward evidence that supports the hypothesis that the mechanism of the coupling is predominantly through-bond (TB) for short-chain biradicals (<10 carbon atoms), while it is mostly through-solvent (TS) for longer chains.<sup>6</sup> Beratan and Onuchic have published a theoretical study of rigid spacing bridges in donor-acceptor molecules that undergo charge separation/recombination<sup>7</sup> and found that the matrix element coupling the donor and acceptor is highly dependent on the geometry and the orbitals of the spacer. To further test the theory, we have initiated a long-term study of scalar exchange couplings in flexible biradicals of novel structure. Biradicals are ideal for the study of such phenomena because they are a direct measurement of the degree of exchange interaction and because they are usually neutral species so that strong solvent/solute interactions are not present. In particular, the effect of localized unsaturation on exchange couplings in these model compounds will help answer questions regarding the rates of electron and energy transfer across a conducting or insulating medium, e.g., in proteins or model compounds,8 and will provide further information about the relative contribution of the TB and TS mechanisms. For this study, we have synthesized two ketones, which upon photolysis yielded biradicals with isolated double bonds between the unpaired electrons. These are shown with their saturated analogues in Scheme I. In this paper we report the results of time-resolved electron paramagnetic resonance (TREPR) experiments on biradicals 1a-4a and compare their magnetic and kinetic properties.

Both TB and TS couplings depend on the chain dynamics of the biradicals.<sup>2</sup> The conformational energies are a function of the external medium, and it is of interest to determine how the solvent might play a role in determining the magnitude of the scalar exchange coupling. In this regard, we have also measured



the changes in TREPR signal from a saturated biradical in solvents of different polarity and viscosity. The solvent effects on the EPR spectra are expected to be small; however, the technique is sensitive, and any effects present may manifest themselves in a variety of ways, such as difference in J couplings (TB or TS), relaxation rates, line widths, or other kinetic parameters.

### **Experimental Section**

All starting materials were obtained from Aldrich and were used as received. 5,9-Cyclododecadien-1-one was prepared from cis,trans,trans-1,5,9-cyclodecatriene by epoxidation using m-chloroperbenzoic acid followed by rearrangement to the ketone, using anhydrous magnesium bromide etherate in refluxing diethyl ether. This keto diene, cyclododecanone, 8-cyclohexadecen-1-one, and cyclohexadecanone were tetramethylated by using lithium diisopropylamide (LDA) and methyl iodide. Both unsaturated tetramethylated products 1 and 2 were mixtures of isomers even



Figure 1. Experimental (left) and simulated (right) time-resolved EPR spectra of unsaturated biradicals and their saturated analogues. These and all subsequent spectra are centered at 3380 G. (A)  $C_{11}$  diene biradical 1a; (B) saturated biradical 3a, (C)  $C_{15}$  monoene biradical 2a; (D) saturated biradical 4a. All spectra were obtained in *n*-octane at boxcar gate delay times of 0.6  $\mu$ s and a temperature of 60 °C. Simulation parameters are listed in Table I.

after repeated column chromatography (pentane/silica gel). The  $C_{12}$  ketodiene 1 was predominantly trans, trans (>75%) with the carbonyl in either the 1- or the 2-position, while the  $C_{16}$  keto monoene 2 was approximately an equal mixture of cis and trans isomers, determined by GC/MS. The TREPR experiments carried out on an apparatus described previously,<sup>9</sup> at concentrations ranging from 0.1 to 0.5 M of starting ketone in the solvent of interest. Higher concentrations were necessary when the experiments were run in single quartz samples tubes instead of flow systems. The low absorbance of the ketones at 308 nm ensured that the concentration of biradicals was not higher than 10<sup>-6</sup> M in any of the experiments.

## **Results and Discussion**

A. Effects of Localized Unsaturation. Experimental and simulated TREPR spectra of the diene 1a and monoene 2a bisalkyl biradicals are shown in parts A and C of Figure 1, with spectra of the saturated analogues 3a and 4a shown for comparison in parts B and D, respectively. Two features of these spectra are noteworthy. It is clear that for both chain lengths, the spectra have more net emissive character when double bonds are included in the chain, and this effect is more pronounced in the diene biradical than in the monoene. Also, there is a significant change in the line width in the spectrum of biradical 1a.

TABLE I: EPR Simulation Parameters<sup>4</sup> for Figures 1 and 6



Figure 2. Energy level diagram for a general nuclear substate  $|\chi\rangle$  of a flexible biradical as a function of applied magnetic field  $B_0$ . Solid arrows represent high probability (triplet-triplet) EPR transitions, while dotted arrows indicate weaker triplet-singlet transitions. Chemical reactions to diamagnetic products are shown to the right, which proceed at different rates for each nondegenerate electronic (and nuclear) spin state.

Computer simulation of spin-polarized biradical EPR spectra has been described in several previous publications,<sup>2c,9</sup> therefore only a brief outline will be given here. The essential features of the model are summarized in Figure 2, where an appropriate basis set is shown, consisting of the direct product of three triplet levels  $(T^+, T^0, and T^-)$  and a singlet level (S) with a symmetryfactored nuclear basis  $|\chi\rangle$ . The spin-spin coupling is shown as 2J and represents the energy splitting between S and T<sup>0</sup>. Mixing of the zeroth-order states via the nuclear hyperfine interaction establishes the initial population of the four levels, which are then redistributed within the manifold of states by spin relaxation. Chemical reaction to diamagnetic products from a given electronic level w proceeds at a rate that is the product of the end-to-end encounter rate  $k_{en}$  and the fraction of singlet character  $\lambda^{w}$  acquired through hyperfine mixing or spin-orbit coupling. This product gives nuclear spin-dependent chemical reaction rates on the order of  $10^6$  s<sup>-1</sup>. Because all of these biradicals have J couplings with a negative sign, as expected from theory,1d conformational dynamics of the biradicals will force the S state to interact on the average more often with T- than with T+, leading to a spectrum that becomes emissive in character over the time scale of a microsecond or so. Larger and more negative J couplings push the S level closer to T- than T<sup>0</sup>, resulting in an even more emissive spectrum in these cases. The simulations shown in Figure 1 satisfactorily reproduce the features observed experimentally, and the values of J and  $k_{en}$  obtained from the fits are listed in Table I. The measured J values indicate that the exchange couplings increase when unsaturated bonds are placed in the chain. The inclusion of  $\pi$ -bonds may affect the TS interaction by forcing the biradical into conformations with different end-to-end distances or it may affect the TB coupling by providing different overlap between the  $\pi$ -bond and the saturated C-H bonds on the adjacent methylene groups. It is not immediately clear which direction the magnitude of J should take, and the focus of the discussion will be an attempt to predict and model the experimental findings.

biradical	spectrum	temp (±3 °C), °C	solvent	J (±5%), MHz	k <sub>en</sub> (±50%), s <sup>-1</sup>	line width ( $\pm 0.2$ G), G
1a	1A	60	n-octane	-1400	$2.5 \times 10^{10}$	2.4
3 <b>a</b>	1 B	60	n-octane	-630	$1.5 \times 10^{10}$	1.8
2a	1C	60	n-octane	-560	$2.2 \times 10^{10}$	2.0
<b>4a</b>	1 <b>D</b>	60	n-octane	220	$2.5 \times 10^{10}$	2.0
5a	4A	25	n-octane	-630	$1.5 \times 10^{10}$	2.0
5a	4B	25	n-hexadecane	$-560 \pm 10\%$	$1.5 \times 10^{10}$	2.1
5a	4C	25	paraffin oil	-630 🛥 10%	$1.5 \times 10^{10}$	3.8
5a	4D	25	benzene	-630	$1.5 \times 10^{10}$	1.8
5a	4E	25	acetonitrile	670	$1.5 \times 10^{10}$	1.2
5a	4F	25	methanol	670	$1.5 \times 10^{10}$	1.4

<sup>a</sup> Hyperfine coupling constants, g-factors, and other kinetic and magnetic parameters are taken from ref 9.



Figure 3. End-to-end distance histograms for a  $C_{12}$  alkane chain at 60 °C using a trans/gauche energy difference of 0.91 kcal mol<sup>-1</sup>. (A) Bonds from C<sub>4</sub> to C<sub>5</sub> and from C<sub>8</sub> to C<sub>9</sub> restricted to the trans configuration; (B) no bonds restricted.

When relating the average value,  $\langle J \rangle$ , obtained from EPR measurements to structural properties of a flexible molecule, it is necessary to have some means of describing the equilibrium conformational distribution in the chains. These are readily calculated from programs that simulate alkane chain dynamics or short polymer chain motions. We use a program based on that of Nairn and Braun<sup>10</sup> which in turn uses Flory's rotational isomeric state model for alkane chain conformations.<sup>11</sup> The program generates random chains along a diamond lattice according to Boltzmann-weighted probabilities. Histograms of end-to-end distances for a particular chain length are obtained after a random sampling of 10<sup>6</sup> chains. By selecting an appropriate function for  $J_{\rm TS}$  with respect to end-to-end distance, an average coupling value  $\langle J_{\rm TS} \rangle$  can be calculated by averaging this function over the

distribution, which is usually plotted as a histogram. In general we do not calculate absolute numbers for J but instead look for relative changes. We have used eq 1 successfully in the past for polymethylene chains,<sup>2c</sup> which is averaged over the histograms according to eq 2. The  $r_i$ 's are the distance "slots" (0.25-Å

$$J = J_0 \exp(-\lambda(r_i - r_0)) \tag{1}$$

$$\langle J_{\rm TS} \rangle = \frac{J_0 \sum_i N_i \exp(-\lambda(r_i - r_0))}{\sum_i N_i}$$
 (2)

resolution in our calculations) from the histograms, the  $N_i$ 's are

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Figure 4. Simplified molecular orbital diagrams for alkyl biradical structures showing the nonbonding orbital splitting (NBOS). For biradicals where the p-orbitals are related by a symmetry operation (left side), the calculated NBOS is proportional to measured J coupling. For biradicals with p-orbitals without such a relationship (right side), the energy difference of the left and right monoradicals ( $\Delta E$ ) is calculated independently, then subtracted from the calculated biradical splitting to give the correct NBOS.

the weighting factors for that distance, and  $J_0$  and  $\lambda$  are adjustable parameters. The value of  $r_0$  is usually taken to be 3.5 Å.

A set of Monte Carlo calculations was run to examine the changes in the distribution of end-to-end distances obtained with one or two rigid bonds in the chain. This was done by restricting the conformation of a  $C_{12}$  alkane chain such that bonds from  $C_4$ to  $C_5$  and from  $C_8$  to  $C_9$  remained locked in the trans position. The results of the calculations are shown in Figure 3. Two features of the histograms are noteworthy: as expected, the all-trans conformational isomer (represented by the distance slot with the longest end-to-end distance) occurs more often in the restricted chain (Figure 3A) than in the unrestricted chain (Figure 3B). Also, fewer conformers of extremely short end-to-end distance (5-10 Å) are obtained for the restricted chain. Since the calculation of  $\langle J_{TS} \rangle$  weights the shorter distances much more than the longer ones, the TS coupling in the restricted biradical should decrease compared with that of its saturated analogue. Using eq 2 with  $\lambda = 1.06 \text{ Å}^{-1}$ ,  $\langle J_{\text{TS}} \rangle$  was computed for the two cases by using the distributions shown in the figure. The restricted chain was calculated to have a lower value of  $\langle J_{TS} \rangle$  by approximately 35%. Less dramatic but similar trends were calculated for chains with one double bond. The experimental results, however, clearly show that  $\langle J \rangle$  increased in the unsaturated system. There are two possibilities: (1) we have only considered the trans, trans isomer of the chain, and the inclusion of any cis bonds could increase  $\langle J_{TS} \rangle$ . The broader line width observed for biradical 1a vs 3a is a potential manifestation of the presence of multiple isomers with different J couplings. It is also possible that a larger through-bond coupling may be responsible for the increase, and a model for this will now be put forward.

The use of ab initio molecular orbital (MO) calculations for direct evaluation of the through-bond contribution to the J coupling is time-consuming and somewhat unreliable because of the size of the molecules and the magnitude of the interactions involved (the measured J couplings are on the order of  $10^{-6}$  eV). If only orbital energy differences are considered, then trends within a series of compounds of similar electronic structure obtained by semiempirical MO calculations should be sufficient to allow the determination of the effect of unsaturation on exchange couplings by the TB mechanism. This assumes that the overlap integral between the orbitals containing the unpaired spins (in this case two nonbonding p-orbitals) is directly proportional to the measured J coupling. As a measure of this interaction, we use the eigenvalue difference of the radical center p-orbitals, called the nonbonding orbital splitting (NBOS), as illustrated in Figure 4. In an asymmetric biradical (one where the p-orbitals cannot be related



Figure 5. Results of PM3 calculations on through-bond couplings in saturated and unsaturated biradicals. See text and Figure 4 for a description of the NBOS term and how it is calculated. (A) 1,6-Hexanediyl in the all-trans conformation; (B) 3-hexene-1,6-diyl in the all-trans conformation; (C) 1,6-hexanediyl with bonds 2 and 4 in the gauche+ and gauche- conformations, respectively; (D) 3-hexene-1,6-diyl in a similar geometry to C.



Figure 6. Experimental (left) and simulated (right) time-resolved EPR spectra of biradical 3a at 25 °C in the following solvents: (A) *n*-octane at a delay time of  $1.0 \ \mu$ s; (B) *n*-hexadecane at  $1.0 \ \mu$ s; (C) heavy paraffin oil at  $1.5 \ \mu$ s; (D) benzene at  $0.8 \ \mu$ s; (E) acetonitrile at  $1.0 \ \mu$ s; (F) methanol at  $1.0 \ \mu$ s. Simulation paramters are listed in Table I.

geometrically by a symmetry operation), the two p-orbitals may already be split due to different local electronic environments. For these cases the eigenvalues of the p-orbitals of the left and right monoradicals are calculated separately and this energy difference ( $\Delta E$ ) is then subtracted from the calculated splitting for the biradical to give the correct NBOS.



Figure 7. End-to-end distance histograms for a  $C_{12}$  alkane chain at 25 °C using trans/gauche rotational energy differences of (A) 0.91 kcal mol<sup>-1</sup> and (B) 0.55 kcal mol<sup>-1</sup>.

The MO calculations are set up in the following manner: first, the energy of the closed-shell conformation of interest is minimized by using molecular mechanics (MM2).<sup>12</sup> Next, the terminal hydrogens are removed to make the biradical, and the H–C–H bond angles are set to 120° for sp<sup>2</sup> hybridized radical centers. We ignore the terminal methyl groups.<sup>13</sup> The dihedral angles formed by each of the two terminal hydrogens with the three endmost carbon atoms are set to  $\pm 90^{\circ}$ . An input file for MOPAC is then created, specifying the PM3 Hamiltonian.<sup>14</sup> Geometry optimization is performed, and the BIRADICAL option in the MOPAC header is invoked, to provide a small amount of configuration interaction in the calculation. Typically 8–12 self-consistent field iterations were needed to achieve convergence. Once the calculation was terminated, the eigenvalues of the two nonbonding p-orbitals are subtracted to give the NBOS. These calculations were not possible for 15 and 16 carbon chain length biradicals, as the difference in eigenvalues was only 1 or 2 meV, well within the noise of a semiempirical MO calculation. The model system chosen for TB calculations is the  $C_6$  biradical (saturated with one double bond in the 3-position), because the couplings are large in this system yet there is enough room along the chain to place an isolated (i.e., nonconjugated) double bond.

The results of the calculations are shown in Figure 5 for two geometries of unsaturated  $C_6$  biradical and their saturated analogues. As expected, for saturated systems the maximum TB coupling is found for the all-trans biradical. The inclusion of two gauche bonds (one gauche+, the other gauche-) lowers the coupling to almost zero. However, as the figure illustrates, the

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presence of the double bond can provide a large coupling, even in the coiled conformation. Although the biradicals are more rigid with double bonds present and TS couplings are found to be diminished, significant interaction by the TB mechanism can still take place. Also, in relation to the conformational analysis above, trans biradicals have a higher probability of being in extended conformations because of their fewer degrees of freedom. Therefore, contributions to  $\langle J_{TB} \rangle$  are more heavily weighted by those chains with longer end-to-end distances.

B. Solvent Effects. It is known that the conformational dynamics of alkane chains are affected by solvent properties.<sup>15</sup> Spectra of biradical 3a run in solvents of different polarities and viscosities are shown in Figure 6 along with simulated spectra. In the case of the light paraffin oil, the poor resolution makes any changes in the spin-spin coupling or encounter rate difficult to observe. Minor changes in the J coupling were observed in methanol and acetonitrile, and we found that the simulations were not extremely sensitive to changes in the encounter rates. In each spectrum the line width changed, sometimes dramatically as in heavy paraffin oil or in very polar solvents such as methanol and acetonitrile. The simulations, using parameters listed in Table I, show that there is a slight increase in J going from hexadecane to methanol and that there is a significant reduction in the line width of the EPR transitions in the more polar solvents. The Monte Carlo calculations again can provide some insight into this. In the previous calculation of histograms of end-to-end distances, the rotational potentials used were taken from an MM2 calculation on gas phase *n*-butane, e.g., 0.91 kcal/mol for the trans/gauche conformational energy difference. Recently rotational potentials for butane in water vs the gas phase were reported and the difference was found to be 0.55 kcal/mol.<sup>16</sup> Lowering this value will have an effect on the end-to-end distance distribution, as demonstrated in Figure 7, which shows histograms using these two different energy gaps. It is clear that, with the lower of the two values, the number of occurrences of the alltrans chain is much less and also the number of chains with endto-end distances of 5-10 Å increases substantially. The value of  $\langle J_{\rm TS} \rangle$  computed by using eq 2 with these histograms increased 60% for the smaller energy gap over the larger one. While the difference between methanol and hexadecane is expected to be smaller than from water to the gas phase, the trend observed in the data is accounted for by this simple model. However, it should be noted that the difference found in the simulations was very slight, falling just outside the error limits.

In heavy paraffin oil, the slow rotational correlation time may not completely average out anisotropic interactions such as the *g*-factor and hyperfine couplings. Additionally, relaxation via dipolar coupling between the unpaired electrons may become important. The decrease in the line width from benzene to acetonitrile and methanol is most likely due to the fact that the chains are more coiled up due to a lower trans/gauche barrier, and the tumbling rate increases for a more spherically shaped molecule, resulting in sharper transitions.

## Summary and Outlook

Our results indicate that isolated double bonds can promote TB couplings due to increased overlap of C-H  $\sigma$ -bonds with the  $\pi$ -bond, while at the same time decrease the TS coupling by forcing the biradicals into more rigid conformations, which will keep the ends farther apart. Our simple model supports the experimental finding that the effect is more pronounced for two

double bonds compared to one. A problem in the data analysis is the fact that the ketoalkenes were mixtures of cis and trans isomers that could not be separated. There are several ways in which this problem could be overcome, for instance by synthesizing samples with different ratios of cis to trans isomers and looking for differences in the measured J coupling. Another would be to synthesize or isolate exclusively one isomer, a more difficult task. In a recent paper,<sup>6</sup> we made extensive use of the temperature dependence of the two mechanisms to gain insight into the problem, and such experiments on these and other unsaturated biradicals are presently being attempted in our laboratory. Despite the limitations of the theoretical models for the two mechanisms, these molecules and the experimental technique provide an excellent way to probe subtle structural and dynamic properties of electronic interactions in flexible chains.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE-9200917, jointly sponsored by the Divisions of Chemistry and Materials Research. The Petroleum Research Fund, administered by the American Chemical Society, through Grant ACS-PRF 23636-G6,4, is gratefully acknowledged for partial financial support.

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