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SPIN EXCHANGE IN NITROXYL BIRADICALS

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Abstract: The electron spin exchange energy has been measured as a function of solvent and of temperature for three nitroxyl biradicals. The effect of temperature can be explained in terms of the flexibility of the molecules. The dependence of the exchange on solvent is complex and not readily interpretable; however, it seems to be related to solvent polarity and the structure of the bridge between radical subunits.

Spin Exchange in Nitroxyl Biradicals

We have studied the effect of solvent and temperature on nitroxyl biradicals I¹, II¹, and III² and found some unusual differences in the way these factors influence the magnitude of the exchange energy (J). S resonances³ are clearly observed under most conditions tested and were used to determine the exchange energies listed in Table I.

For biradicals I and II in the extended conformation⁴ the distances between the nitroxyl groups and their relative orientations should be essentially identical, but the exchange energy for II is consistently smaller than for I. This comparison is valid down to -60°C (in CHCl_3) and therefore is probably not a result of the greater stiffness of II due to amide resonance (see below). For III the nitroxyl groups are held 1 to 2 Å closer together than in I or II, and their relative orientation is such that greater overlap of the molecular orbitals containing the unpaired electrons would be expected. Thus, if direct overlap is important in determining the exchange magnitude in those biradicals, then one would expect to observe a much larger exchange in III than in I or II, which is generally not the case. These observations strongly support a participation of the connecting bridge in determining the exchange energy as suggested by Glarum and Marshall.³ They are not consistent, however, with the suggestion that the exchange through the joining structure decreases with the number of sigma bonds separating the radical centers,³ since the shortest path for such exchange in III is one bond less than in I or II while the observed exchange can be smaller for III.

I

II

III

XBL 746-5195

The effect of solvent on the exchange energy is similar for biradicals I and II, $\underline{J}$ tending to increase with increasing solvent polarity (for example, as measured by the Kosower Z value⁵). The hyperfine interaction, $\underline{a}$, also changes in a consistent manner with solvent polarity (Table I), and it would seem likely that the solvent dependence of $\underline{J}$ is related to the changes in electron density distributions indicated by the changes in $\underline{a}$.⁶ In contrast to I and II, III shows a decrease in exchange energy with increasing solvent polarity. The greatest variation in $\underline{J}$ occurs in the solvents hexane, xylene, and chloroform, the other solvents examined all giving similar results, indicating that simple spin density distribution changes in the nitroxyl groups are not solely responsible for the solvent effects. The opposing trends observed for these biradicals considerably complicate the discussion of effects of solvent on the exchange energy. Combined with the observed effects of temperature (see below), these results negate the suggestion that solvent affects the most probable conformations of the biradicals and thereby the exchange.³ Our observations rather seem to emphasize the importance of the connecting bridge in determining $\underline{J}$ as a function of solvent polarity.

The effect of temperature on exchange in these biradicals is also dependent on the structure and generally reflects the flexibility of the molecules. For I above 30°C the exchange energy appears to modulate over a range of values resulting in extreme broadening of the S resonances. This observation has been reported previously and interpreted in terms of increased flexing of the molecule at higher temperatures.³ In CHCl_3 , as the temperature is decreased to -60°C, the S resonances sharpen progressively, indicating that molecular motion is still important below 0°C.

In addition, the exchange energy determined from the positions of the S resonances increases with decreasing temperature at a rate of 0.075 G/°C (CHCl_3). In contrast, for II the S resonances begin to broaden at temperatures greater than 100°C, yet remain observable up to 200°C in xylene. Biradical II thus appears to be considerably less flexible than I, probably due to amide resonance in II. This would indicate that rotation about the carbonyl-oxygen linkage is important in creating the incoherence of $\underline{J}$ for biradical I at higher temperatures. As the temperature is decreased below 20°, the exchange energy measured from the S resonance positions increases at a rate of 0.025 G/°C (CHCl_3). Unlike biradical I, however, the S resonances tend to broaden slightly with decreasing temperature.

For biradical III, flexing should consist only of limited rotation about the C_4^{N} -N bond and of flexing in the 5- and 6-membered rings. Accordingly, we observe no broadening of the S resonance lines up to 200°C in xylene or down to -60°C in carbon disulfide. The twisting about the C_4^{N} -N bond is sufficiently great that it should have a quite drastic effect on the direct overlap of the unpaired electron distributions. Unless this motion is fast over the entire temperature range examined and therefore results in an average exchange, these observations again indicate that simple direct exchange is of little importance. In contrast to I or II, we observe for III a nearly linear increase in $\underline{J}$ with increasing temperature of 0.08 G/°C in xylene (20 to 200°C), 0.074 G/°C in chloroform (20 to 150°C), and 0.092 G/°C in carbon disulfide (-60 to 20°C). For all three biradicals studied here, the small changes in $\underline{J}$ with temperature could be due to rapid conformational changes in the molecules.

However, one must also consider the possibility that these changes reflect changes in solvation with temperature, since solvent is important in determining the exchange energy.

These results support the idea that the exchange energy in a biradical is strongly influenced by the chemical nature of the connecting bridge in a manner not simply related to the distance between the nitroxyl groups or their relative orientation. For biradical III the results appear to be inconsistent with either a simple indirect (through bond) or direct (through space) exchange mechanism since one would expect the exchange to increase with the electron density on nitrogen (i.e., with increasing a) as is seen for I and II. The exchange thus seems a complex function of the biradical structure.

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Footnotes

(1) E. G. Rozantsev, V. A. Golubev, M. B. Neiman, and Yu. V. Kokhanov, Izv. Akad. Nauk SSSR, Ser. Khim., 3, 572 (1965).

(2) This compound was originally reported by Joss et al., J. Org. Chem., 37, 2015 (1972) as N-(1-oxyl-2,2,6,6-tetramethylpiperidyl-4)-N'-(1-oxyl-2,2,6,6,-tetramethyl-4-methoxycarbonylpiperidyl-4) urea; however, analytical, mass spectral and nmr data on the compound or amine precursor indicate its correct structure is that of Biradical III. The cyclization with loss of methanol is easily envisioned under the reaction conditions used. The weaker set of S resonances noted in the paper by Joss et al. correspond exactly to the symmetrical urea II in all solvents and are most likely due to a small amount of this impurity which can easily be formed in the reaction. It should also be noted that the calibration of the esr sweep is incorrect in the Joss paper, which explains the differences in our a and J values.

(3) S. H. Glarum and J. H. Marshall, J. Chem. Phys., 47, 1374 (1967).

(4) H. Lemaire, J. Chim. Phys., 64, 559 (1967).

(5) E. M. Kosower, J. Amer. Chem. Soc., 80, 3253 (1958).

(6) H. Hayat and B. L. Silver, J. Phys. Chem., 77, 72 (1973).

Table I. Effect of Solvent on Biradicals I-III at 22°C

Solvent	Z*	I		II		III	
		<u>a</u>	<u>J</u>	<u>a</u>	<u>J</u>	<u>a</u>	<u>J</u>
hexane	60.0	15.2	24.3	15.2	15.8	14.9	43.4
xylene	63.0	15.2	27.1	15.2	18.6	15.1	26.5
acetone	65.7	15.6	30.3	15.5	18.2	15.2	19.4
DMF	68.5	16.0	28.9	15.8	18.7	15.4	16.9
DMSO	71.0	15.7	28.8	15.8	17.2	15.4	16.2
MeOH	83.6	16.0	28.7	16.1	17.4	15.8	18.4
H ₂ O	94.6	17.0	38.6	17.1	23.4	16.7	14.8
CHCl ₃	63.2	15.8	35.6	15.9	24.2	15.5	37.4
HOAc	79.2	16.2	34.7	16.4	20.6	15.9	20.3

* Kosower Z value.⁵

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