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Unexpected Influence of Viscosity on Intramolecular Spin Exchange in Nitroxide Biradicals

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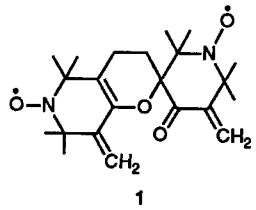
The spin exchange dynamics and the rotational mobility of rigid-frame nitroxide biradicals have been studied by EPR; despite the intramolecular character of the exchange, its rate correlates with molecular mobility, being damped in viscous media, thus proving that even the simplest intramolecular reactions are controlled by molecular dynamics.

Electron paramagnetic resonance (EPR) offers a unique opportunity to study simultaneously both the molecular dynamics and the reaction kinetics of free radicals.[1] Such studies have already produced rather unexpected results concerning correlations between molecular mobility and the rate of monomolecular chemical conversion.[1,2] Electron spin exchange is considered to be the simplest model of electron transfer processes, the latter being significant for many chemical and biochemical reactions. Hence, parallel observation of both spin exchange and molecular mobility may provide important information about the characteristics of electron transfer in condensed media.

A correlation between the rate of rotation and that of intramolecular spin exchange was first observed[3,4] for long-chain flexible nitroxide biradicals.[5] In this case direct spin exchange may occur through collisions of nitroxide fragments of the same molecule. So far, the linear correlation between τ_{ex}, the characteristic time of exchange, and τ_c, the time of molecular reorientation may arise from a correlation between the different modes of motion. This agrees with numerous experimental data obtained using high frequency (2 mm wave band) EPR and indicates that rotational frequencies around different molecular axes differ only in the numerical coefficient.[2]



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A special case is indirect exchange within rigid-frame biradicals, where any influence of molecular motion on spin exchange seems to be excluded. Several rigid-frame nitroxide biradicals are presently known,[5] from among which we chose to study compound **1**. The EPR spectra of **1** were interpreted in ref. 6. In

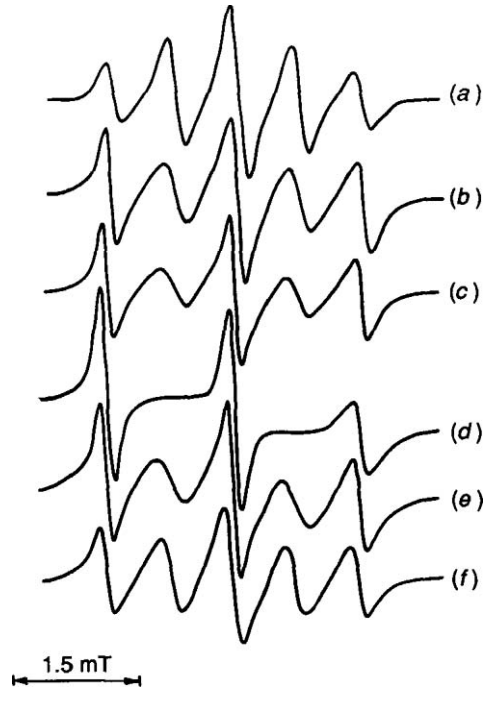

Fig. 1 EPR spectra of biradical **1** in different media. (*a*) Hexane, 20 °C; (*b*) hexane–Vaseline (1:3), 20 °C; (*c*) (1:5), 20 °C; (*d*) Vaseline, 20 °C; (*e*) 40 °C; (*f*) 60 °C.

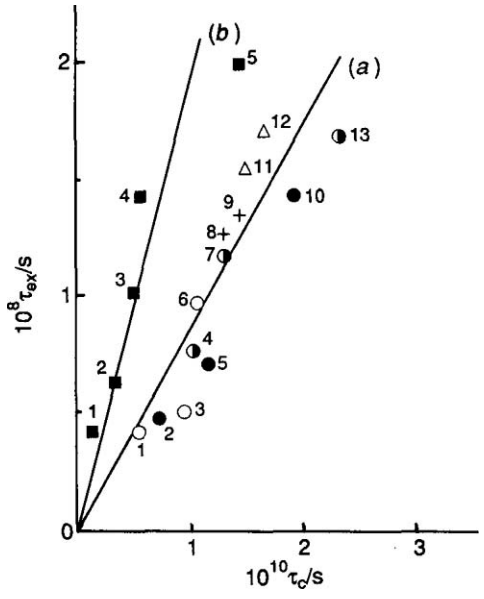

Fig. 2 Correlation between τ_{ex} and τ_c for biradical **1**. (*a*) Both composition and temperature varied: 1, hexane–vaseline oil (1:3), 60 °C; 2, (1:3), 50 °C; 3, (1:5), 60 °C; 4, (1:3), 40 °C; 5, (1:5), 50 °C; 6, vaseline oil, 60 °C; 7, hexane–vaseline oil (1:5), 40 °C; 8, (1:3), 30 °C; 9, (1:5), 30 °C; 10, vaseline oil, 50 °C; 11, hexane–vaseline oil (1:3), 20 °C; 12, (1:5), 20 °C; 13, vaseline oil, 40 °C. Symbols (○, ●, ◑, +, ▲) denote measurements made at the same temperature with a different composition. (*b*) (■) temperature only varied in decanol: 1, 60; 2, 50; 3, 40; 4, 30; 5, 20 °C.

nonviscous solution the spectrum is a quintet with relative intensities 1:2:3:2:1. It exhibits strong exchange between the NO-fragments as for a single fragment, but a triplet (1:1:1) signal is observed. The temperature dependence of the line width is rather weak, suggesting the presence of indirect spin exchange through the chain of σ- and π-bonds.

We have studied the EPR spectra of **1** in viscous solutions in Vaseline and long-chain aliphatic alcohols. Typical spectra are presented in Fig. 1. They demonstrate the marked broadening of the biradical lines when viscosity increases at constant temperature (*i.e.* as the composition of the hexane + Vaseline mixture is changed). In pure Vaseline, a triplet spectrum is observed, corresponding to an absence of intramolecular spin exchange. When temperature was increased, quintet biradical spectrum appeared with alternating line width, but with integral intensities corresponding exactly to 1:2:3:2:1. Similar changes were observed in ethanol, butanol, octanol and decanol, with the exchange rate decreasing in that series. Thus, the intramolecular exchange rate in **1** decreases as the viscosity of the medium increases. This was quite unexpected, considering the rigid frame of molecule **1** and the absence of an obvious connection between molecular mobility and exchange rate.

We propose that for each act of elementary spin exchange a certain rehybridisation of molecular orbitals is needed, involving certain displacements of atomic positions. The surrounding molecules, forming the walls of a kinetic cage, prevent such displacements, thus coupling the motional coordinates with the reaction coordinates. In other words, an elementary spin exchange act is controlled by the reorganisation of the cage, including biradical and nearby surrounding molecules.

The spectra in Fig. 1 demonstrate not only the broadening of the biradical component signal as viscosity increases, but also that the low field component broadens noticeably more quickly. This is caused by slower modulation of the anisotropic hyperfine interaction with reorientational (or rotational) molecular motion.[3,4] This enables us to find independently the parameters τ_{ex} and τ_c of the exchange and reorientation rates.[3,4] The experimental data thus obtained are presented in Fig. 2, demonstrating direct proportionality [eqn. (1)].

$$\tau_{ex} = \alpha\tau_c \quad (1)$$

As a phenomenological explanation of the strong correlation between motional and reaction rates, the model of indirect cage effect cited earlier[2] predicts a simple approximate relationship [eqn. (2)], where τ_s is the time of reaction in viscous media, τ_f is

$$\tau_s = \tau_f + \alpha\tau_c \quad (2)$$

the same for an ideal nonviscous fluid and

$$\alpha = \alpha_0 \exp(E_f/2RT) \quad (3)$$

E_f being the activation energy for an ideal reaction and α_0 being the reaction coefficient, depending on the number of reorientation steps corresponding to one reaction event.

For a very fast process, such as spin exchange, one may assume $E_f \approx 0$ and $\tau_f \ll \tau_c$, then eqn. (2) converts to eqn. (1) with $\tau_{ex} = \tau_s$ and $\alpha = \alpha_0$.

In our experiments we changed τ_c by changing either the temperature or the composition of the hexane–vaseline mixture [Fig. 2(*a*)], but we still obtained the linear relationship (1) with $\alpha_0 = 85$. For alcohol matrices $\alpha_0 \approx 200$ [Fig. 2(*b*)]. One may conclude that about 10^2 reorientation steps are needed for only one act of spin exchange to occur.

The rather simple model outlined above does not work for experiments involving cooling down low viscosity solutions of **1** in ethanol, hexane or toluene. At 190–210 K the spectra of **1** remain as quintets with no detectable broadening of the biradical components. The amplitudes of the extreme outside components also remain the same, indicating that neither reorientational nor rotational frequency decrease. This observation probably relates to the specificity of the microscopic structure of the cage of the rigid biradical **1**, since for other more flexible biradicals a smooth decrease in reorientation frequencies is observed under similar conditions.[3,4] We propose that the necessity for a particular molecular organisation of small solute molecules around **1** is responsible for the contamination of high molecular mobility at lower temperatures as well as for the high rate of intramolecular spin exchange.

The interpretation of the above results may appear rather unexpected in comparison with the usual models of direct and indirect spin exchange. The earlier conclusions about indirect exchange in biradical **1**[5,6] now appear to be invalid, as the exchange-coupled quintet spectra are temperature independent only in the nonviscous solutions used in ref. 6. Under the experimental conditions of ref. 6, we also observed temperature-independent quintets, but in more viscous media spectral changes are evident (see Fig. 1).

One might speculate about the possibility of complete twisting with resulting direct spin exchange in molecule **1**, but a more reasonable explanation seems to be that intramolecular spin exchange occurs in slightly excited conformational states. The 'rigid' structure of **1** is indeed somewhat flexible and its flexibility is controlled by the viscosity of the surrounding medium. In addition to other experiments on intramolecular reactions,[1–4,7,8] the present data indicate that even the simplest electron rearrangements within a single molecule are actually controlled by molecular dynamics when they proceed in condensed media.

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