

On the mechanism of spin exchange in long-chain nitroxide biradicals

by V. N. PARMON, A. I. KOKORIN, G. M. ZHIDOMIROV
and K. I. ZAMARAEV

Institute of Chemical Physics, Academy of Sciences
of the U.S.S.R., Moscow B-334

(Received 24 October 1974)

It is shown that the E.S.R. spectra of long-chain nitroxide biradicals represent the superposition of the spectrum of the non-reacting radical moieties in the elongated conformation and of that of the cage where the radical moieties are close together and can interact with each other. Inside the cage a fast intramolecular motion is observed. Some thermodynamic parameters of the cage as well as thermodynamic parameters of the motion inside the cage are calculated from the experimental E.S.R. spectra of four biradicals.

The spin exchange between the radical centres of the nitroxide biradicals with the long chains (e.g. 8-10 and more fragments of $-\text{CH}_2-$) is known to occur only via their direct impacts [1-8], and the typical five-lines E.S.R. spectra (figure 1) indicate the large value ($|J| \gg a$, $-a \approx 3 \times 10^8$ rad/s—the hyperfine constant) of the exchange integral J during the collision [8, 9]:

When the temperature decreases a noticeable broadening of the lines 2 and 2' (figure 1) are observed as well as the diminution of their relative intensities up to their disappearance. Such a behaviour of the E.S.R. spectra was treated on the framework of the model of fast exchange [9] as a consequence of an energetical preference of those conformations, in which the molecules were elongated and $J=0$ [1].

However, it has been shown recently [10, 11] that for some nitroxide biradicals the model of slow but not of fast exchange was valid. For this reason it seemed interesting to re-analyse the mechanism of spin exchange in the long-chain nitroxide biradicals.

We have studied the E.S.R. spectra of the nitroxide biradicals I-IV; the synthesis and physical properties of these biradicals are described [2, 3, 7]. The E.S.R. spectra were obtained from degassed solutions with the Varian E-4 spectrometer; the concentration of the biradicals was less than 10^{-3} M. The temperature was controlled within the accuracy of $\pm 1^\circ$. The typical temperature changes in the E.S.R. spectra are shown in figure 1.

This fact attracts attention that the features, which are typical both for the spectra with the fast exchange and for those with the slow exchange [10, 11], are observed simultaneously in the E.S.R. of the biradicals under consideration. Indeed, considerable narrowing of lines 2 and 2' when the temperature increases indicate unambiguously the fast modulation of the exchange interaction by an

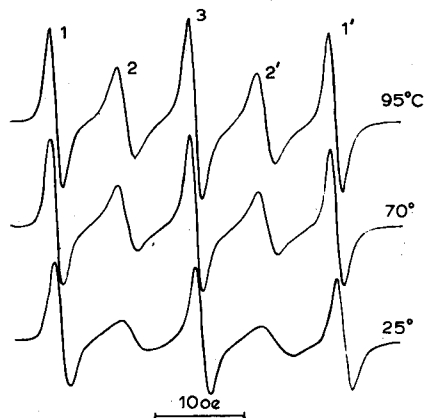
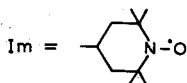
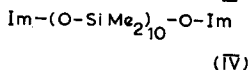
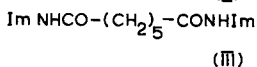
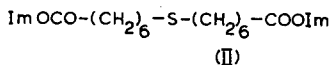
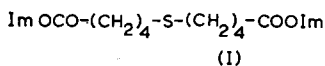


Figure 1. The temperature changes in the E.S.R. spectrum of the biradical IV, dissolved in DMSO.



intramolecular motion. However, at the temperatures when the widths of lines 2 and 2' are close to those of lines 1 and 1', the ratio of line intensities differs essentially from 1 : 2 : 3 : 2 : 1 (see figure 1) which is predicted by the model of the biradical with two conformations and with the strong fast exchange [9, 10] and is observed in practice for many biradicals with the really fast exchange (see, for example, [8]). For this reason the observed distribution of line intensities indicates the mechanical superposition of the spectra of different conformations, i.e. the presence of the slow exchange.

The observed behaviour of the spectra can be simply explained if we assume for the biradicals discussed the model with more than two conformations.

Indeed, let us suppose that in addition to the 'elongated' conformation A with $J_A = 0$ there are yet two conformations B and C in which the radical fragments are drawn together in such a way that $J_B = 0$ and $|J_C| \gg a$ (figure 2). This model describes, e.g., the situation when the nitroxide fragments occur in the same 'cage' of the solvent, but can either interact (the conformation C) or not (the conformation B) depending on their mutual orientation. If the average

lifetimes of the radical fragments inside the cage τ_C and outside the cage τ are sufficiently long ($a \max(\tau, \tau_C) > 1$), a superposition of the E.S.R. spectrum of the cage and that of the separate radicals will be observed (with the statistical weights $\tau_C/(\tau + \tau_C)$ and $\tau/(\tau + \tau_C)$ respectively). If now the movement of the radical fragments inside the cage is fast, the E.S.R. spectrum of the cage will be described by the model of fast exchange.

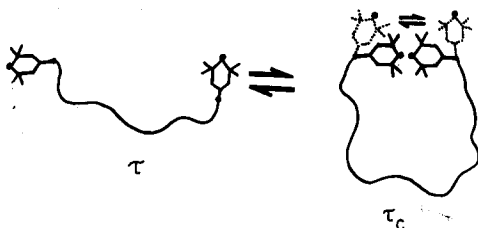


Figure 2. The scheme of the proposed mechanism of the intra-molecular spin exchange for long-chain biradicals.

In the framework of this three-conformational model the variation with the temperature in the widths of lines 2 and 2' can be ascribed to the variation of the modulation conditions for the exchange interaction inside the cage, while the observed distribution of the line intensities can be explained as a result of the superposition of the E.S.R. spectrum of the cage and of that of the radicals outside the cage.

Note that in the same solvents and at the same temperatures the widths of lines 2 and 2' are the same for the biradicals of similar structures, though they have different chain length. This fact supports the conclusion that the width of these lines is determined by the movement of the nitroxide fragments solely inside but not outside the cage. At the same time the relative intensity of these lines decreases when the length of the chain increases in agreement with the expected diminution of the ratio τ_C/τ and thus of the statistical weight of the cage in these conditions. As an illustration the E.S.R. spectra of the biradicals I and II dissolved in dimethylsulfoxide (DMSO) are compared in figure 3; these biradicals are different only in the length of the chain.

The model proposed allows one to obtain the thermodynamical parameters for the intramolecular processes in the long-chain biradicals. Since the cage is described by the single effective conformation with the strong fast exchange that is $|J| \gg a$ [10]), the ratio τ_C/τ is easily calculated from the experimental E.S.R. spectra by comparison with the integral intensities I_1 and I_2 of the lines 1, 1' and 2, 2' respectively. Indeed

$$I_1/I_2 \approx d_1(\Delta H_1)^2/d_2(\Delta H_2)^2, \quad (1)$$

where d_1 and d_2 are the amplitudes, ΔH_1 and ΔH_2 are the widths of lines 1 and 2 (averaged over the lines 1 and 1' or 2 and 2').

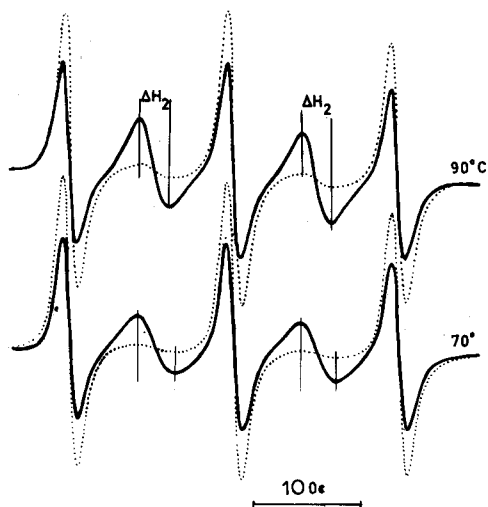


Figure 3. The comparison of the E.S.R. spectra of the biradicals I (the solid curve) and II (the dotted curve) in DMSO.

Noting that the observed E.S.R. spectrum is the superposition of two spectra, we get

$$\tau_C/\tau = \frac{3(I_2/I_1)}{2 - (I_2/I_1)}. \quad (2)$$

The values τ_C/τ calculated from (1) and (2) are presented in figure 4 (a) in the Arrhenius axes. It is seen that as a rule τ_C/τ increases slightly with temperature. This means that the relative energy of the elongated conformation is somewhat less than that of the 'collisional' one; such a difference in energies depends strongly enough on the solvent. So, even for such similar solvents as toluene and benzene there is an observable difference in ΔS due to different solvation of biradicals (see the table).

It must be noted that the measured values of τ_C/τ can be strongly affected by the conditions of E.S.R. measurements, e.g. because of the high sensitivity of the observed amplitudes of the very narrow principal E.S.R. lines to the amplitude of low frequency modulation. As it is seen from figure 4 (a) even a small excess of the modulation power can provide the qualitative difference in the measured dependence of τ_C/τ on the temperature (the dotted line represents the distorted values of τ_C/τ for biradical I in toluene).

The analysis of the lines 2 and 2' narrowing with the temperature allows one to make some conclusions about the motion of the radical fragments inside the cage. In the case of the fast modulation of the exchange interaction the exchange broadening $1/T_2$ of the lines 2 and 2' is described by the expression

$$1/T_2 = \frac{1}{2} a^2 \tau_{\text{eff}}$$

where τ_{eff} is a complex combination of the modulation parameters [8, 9]; the value of τ_{eff} is close to the longest of the characteristic times of the motion inside

the cage. For the Lorentzian lines [8]

$$a\tau_{\text{eff}} \approx 4.13 \times (\Delta H_2 - \Delta H_1)/a. \quad (3)$$

The values of $a\tau_{\text{eff}}$ for the biradicals discussed calculated with the use of the formula (3) are presented in the Arrhenius axes in figure 4 (b).

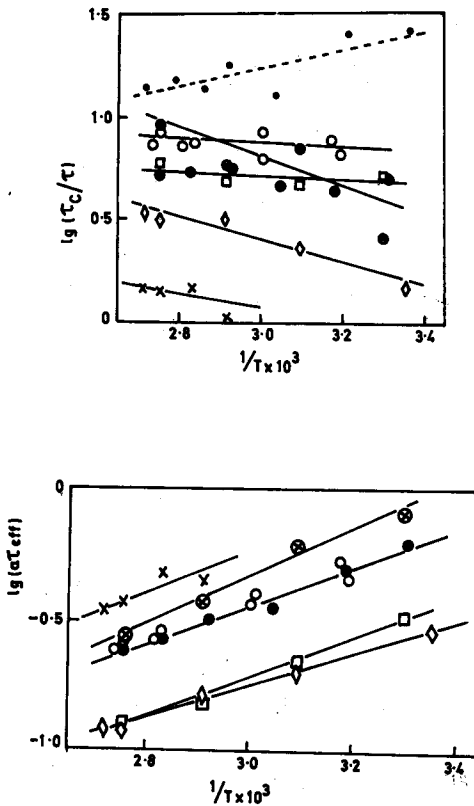


Figure 4. τ_c/τ (a) and $a\tau_{\text{eff}}$, (b) as a function of the temperature. \otimes : I in DMSO, \circ : I in benzene, \bullet : I in toluene, \times : II in DMSO, \square : III in benzene, \diamond : IV in DMSO.

Biradical	Solvent	ΔH (kJ/mol)	ΔS (J K ⁻¹ /mol)	$-\lg(\tau_0) \pm 1$ (τ_0 in sec)	$\epsilon \pm 2$ (kJ/mol)
I	Benzene	0.2 ± 2	17.3 ± 3	10.9	13.5
I	Toluene	0.2 ± 2	12.2 ± 3	11.1	14.3
I	DMSO	11.3 ± 6	49.5 ± 8	11.6	17.6
II	DMSO	5.5 ± 4	8.4 ± 8	11.1	15.5
III	Benzene	0.2 ± 2	12.2 ± 4	11.5	14.7
IV	DMSO	10.1 ± 2	37.8 ± 4	11.0	12.2

Thermodynamic properties of biradicals in various solvents.

Supposing the Arrhenius dependence between τ_C/τ , τ_{eff} and the temperature T is

$$\tau_C/\tau = \exp \{ \Delta S/R - \Delta H/RT \},$$

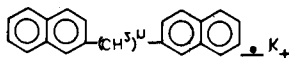
$$\tau_{\text{eff}} = \tau_0 \exp \{ \epsilon/RT \},$$

one can calculate the values of the entropy ΔS and of the enthalpy ΔH of the cage as well as of the parameters τ_0 and ϵ from the data of figure 4 (see the table).

It is interesting to note that the values obtained ($\tau_0 \sim 10^{-11}$ s) differ slightly enough for the various biradicals studied and have the order of magnitude which is typical for intramolecular rotations; the activation energy ϵ of such rotations depends strongly on the nature of the biradicals and on the solvent.

Thus the E.S.R. spectra of the long-chain nitroxide biradicals allow one to observe directly and to study quantitatively the dynamics of intramolecular collisions of the molecular fragments separated by many chemical bonds. Such data seem to be important for understanding the mechanism of the elementary chemical reactions of macromolecules. In this connection it is interesting to note that the cage model, which is often used to describe the kinetics of bimolecular reactions in liquids and solids, is valid for the intramolecular spin exchange processes in the long-chain biradicals too.

It seems that a similar model can be used to describe the electron transfer between the ends of a long molecule in the bridge-type anion-radicals. It has been demonstrated recently [12] that the E.S.R. spectra of the anion-radical



at $n \geq 12$ possessed the features of the slow exchange spectra. On the grounds of the results obtained for the spin exchange it seems interesting also to look for the influence on the E.S.R. spectra of the long-chain anion-radicals of the fast movement of the aromatic fragments during their intramolecular collision.

The theoretical analysis of the E.S.R. spectra of the biradicals with the three conformations will be given in detail in a future paper.

The authors express their thanks to Professor E. G. Rozantsev and Dr. A. B. Shapiro who kindly provided the samples of the long-chain nitroxide biradicals. They are also grateful to the referee for comments which led to a significant revision of this work.

REFERENCES

- [1] RASSAT, A., 1971, *Pure appl. Chem.*, **25**, 623.
- [2] BUCHACHENKO, A. L., GOLUBEV, V. A., MEJIDOV, A. A., and ROZANTSEV, E. G., 1965, *Teoret. exp. Khim.*, **1**, 249 (in Russian).
- [3] SHAPIRO, A. B., BAJMAGAMBETOV, K., GOLDFELD, M. G., and ROZANTSEV, E. G., 1972, *J. org. Khim.*, **8**, 2263 (in Russian).
- [4] SHAPIRO, A. B., SUSKINA, V. I., FJODOROVA, V. V., and ROZANTSEV, E. G., 1970, *Izvestia (seria khimicheskaja)* (in Russian), p. 694.

- [5] ROZANTSEV, E. G., GOLUBEV, V. A., NEIMAN, M. B., and KOKHANOV, YU. V., 1965, *Izvestia (seria khimicheskaja)* (in Russian), p. 572.
- [6] BUCHACHENKO, A. L., RUBAN, L. V., and ROZANTSEV, E. G., 1967, *Radiospectroscopical and Quantum Mechanical Methods in Structural Investigations* (in Russian) (Moscow), p. 167.
- [7] ROZANTSEV, E. G., 1970, *The Free Iminoxyl Radicals* (in Russian) (Moscow).
- [8] BUCHACHENKO, A. L., and VASSERMAN, A. M., 1973, *The Stable Radicals* (in Russian) (Moscow).
- [9] LUCKHURST, G. R., 1966, *Molec. Phys.*, **10**, 543.
- [10] PARMON, V. N., and ZHIDOMIROV, G. M., 1974, *Molec. Phys.*, **27**, 367.
- [11] PARMON, V. N., KOKORIN, A. I., ZHIDOMIROV, G. M., and ZAMARAIEV, K. I., 1973, *Molec. Phys.*, **26**, 1565.
- [12] SHIMADA, K., MOSHUK, G., CONNOR, H. D., CALUWE, P., and SZWARE, M., 1972, *Chem. Phys. Lett.*, **14**, 396.