Russian Chemical Reviews **62** (6) 509 – 526 (1993) © 1993 Russian Academy of Sciences and Turpion Ltd

UDC 541.515:541.124

Relation between molecular and chemical dynamics for elementary radical reactions in viscous media

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Abstract. Experimental data on the effect of viscosity on the kinetics of elementary chemical reactions of free radicals in solid matrices and viscous solutions are analysed. The dynamic effects in EPR spectroscopy are used for the simultaneous investigation of molecular and chemical dynamics. The intramolecular transformations in free radicals and the spin exchange in biradicals are considered. It is shown that the rates of such intramolecular reactions are controlled by the molecular dynamics of the chemical cage. The bibliography includes 58 references.

I. Introduction

The influence of the viscosity of the medium on the rates of chemical reactions is one of the 'classical' effects in physicochemical kinetics. However, new results, significantly supplementing and modifying the existing ideas, have been obtained in recent years. These ideas refer to diffusion-controlled reactions. If the direct chemical step is rapid, then the rate of a bimolecular reaction is determined by the frequency of the diffusional encounters of the reactants in the 'cage', while the rate of unimolecular decomposition is determined by the frequency of the release of the products from the cage. It has been shown comparatively recently that slow bimolecular reactions, for which the duration of the chemical step is many orders of magnitude greater than the duration of the diffusional approach, can also be controlled by the viscosity of the medium. This can be explained most simply by considering the rotational diffusion of molecules, already involved in an encounter within the cage, as the rate-limiting stage of the process: in this case, the rate of the reaction is proportional to the rotational diffusion coefficient (as in the usual diffusion-controlled processes, the rate is proportional to the translational diffusion coefficient) and is determined unambiguously by the viscosity of the medium. The influence of the viscosity of the medium on a series of intramolecular processes, which cannot be controlled by rotational mobility, has been observed experimentally in recent years. This necessitates the consideration of the microscopic (at the level of intramolecular dynamics) relation between the viscosity of the medium and the rates of chemical reactions. It was found that the viscosity influences intramolecular processes, which at first sight do not require any intramolecular rearrangements (for example, spin exchange or electron transfer in non-polar media).

The present review is not concerned with 'classical' diffusion-controlled reactions and its subject is only slow bimolecular reactions of free radicals and their intramolecular transformations. As will be shown below, it is precisely in the case of free radicals that the EPR method makes it possible to investigate simultaneously the reaction rates and the molecular mobilities of the reactants, i.e. to compare the frequencies of the molecular motions, whose relation with the viscosity of the medium is evident, with the frequencies of the chemical steps. Attention is concentrated on the analysis of the experimental results obtained in recent years.

II. The influence of molecular mobility on the kinetics of bimolecular reactions of free radicals

Together with the usual cage effect, consisting in the fact that the relatively immobile species comprising the medium prevent the release of radicals into space, in the case of radical reactions in solid matrices there exists the so called indirect cage effect leading to the retardation of the bimolecular chemical reaction proper.[1] It cannot be explained by diffusional limitations, since the observed bimolecular reaction rate constants are several orders of magnitude lower than the rate constants for the encounters of the reactants. The first effects associated with the influence of the mobility of the medium on the kinetics of slow bimolecular reactions in polymers were observed by Roginskii and coworkers[2–4] and Denisov and coworkers[5–9] The molecular mobility in polymers changed as a result of the change in the external pressure and the plasticisation of the polymer by chemically inert solvents. The interaction of the phenoxyl radical PhO$^{\cdot}$ with a polymeric peroxide, i.e.

$$\mathrm{PhO^{\cdot}} + \mathrm{ROOH} \xrightarrow{k_1} \mathrm{PhOH} + \mathrm{ROO^{\cdot}}, \qquad (1)$$

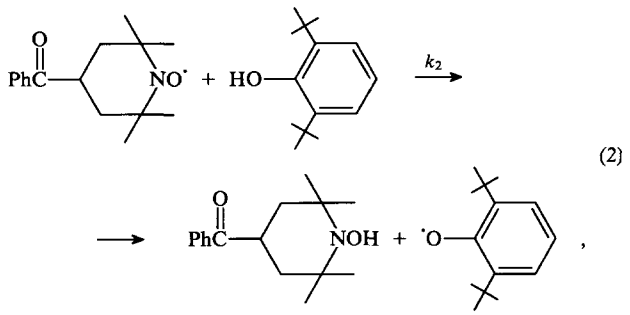
has been investigated and it has been shown that in polypropylene the reaction is accelerated on plasticisation.[2] The increase in the rate constants k_1 in the polymer is accompanied by a decrease in

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Received 18th January 1993
Uspekhi Khimii **62** (6) 547 – 564 (1993); translated by A K Grzybowski

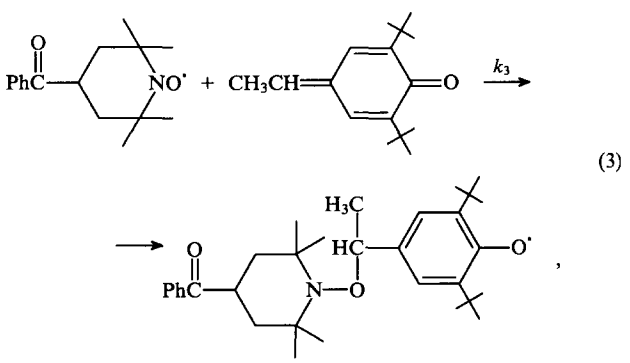
the activation energy and in the pre-exponential factor in the Arrhenius equation.

It has been shown[5,8] that the rate constants for bimolecular reactions involving the abstraction of a hydrogen atom by a nitroxyl radical from 2,6-di-*tert*-butylphenol, i.e.



(2)

and the addition of the same radical to the double bond of α-methyl-2,6-di-*tert*-butylmethylenequinone, i.e.



(3)

in plasticised polymers are determined unambiguously by the molecular mobility—the frequency of the rotation of the nitroxyl-radical involved in the reaction.

Another characteristic feature of the radical reactions in polymers is the levelling of the reactivity, i.e. rapid reactions are retarded much more markedly on passing to the solid phase. The levelling is manifested quantitatively by the fact that, for the same chemical reactions (occurring in the kinetic region), the rate constants in the solid phase (k_s) differ much less than those in the liquid phase (k_f) and that the relation $k_s \propto k_f^{1/2}$ holds approximately.[10] If the frequency of the rotation of the spin probe is measured in the same matrices, then the relation $k_s \propto \nu_c$ is seen to hold in the range of frequencies corresponding to the rotational mobility ($\nu_c = 10^8 - 10^9\ s^{-1}$). At higher frequencies, this type of relation is not observed.

If one uses indirect data, then the correlation between the rate constant and the mobility of the medium can be found in a much greater number of experiments. For example, a linear relation has been observed[11-13] between $\ln k_s$ and the fraction of the fluctuation volume f. The study of the rotational mobility of spin probes has shown that the same relation holds between $\ln \nu_c$ and f,[14] so that one may claim that in such cases a correlation is observed between the chemical reaction rate constant and the frequency of molecular reorientations. Data indicating the pressure dependence of k_s and ν_c can be compared similarly.[14-16] These relations are of the same type:

$$\ln k_s, \ln \nu_c \propto -p/c,$$

where p is the pressure and c a coefficient characterising the change in the modulus of bulk compression with increase in pressure. Hence it also follows that $k_s \propto \nu_c^m$.

Thus the early experiments designed to investigate the influence of molecular mobility on the kinetics of elementary chemical reactions demonstrated the effectiveness of the spin probe method for understanding the kinetics of reactions in polymers.

Bimolecular substitition reactions in solid matrices (inhibition, oxidation chain propagation, etc.) are of special interest to investigators of the structure and stabilisation of polymers.[17] It is then necessary to develop reliable methods for the prediction of reactivities in solid phase reactions, the elementary rate constants of which in the liquid phase are known. It has been shown in relation to the substitution reaction (2)[18] that measurement of the molecular mobility of the spin probe in a solid polymer and the knowledge of the reaction rate constant in the liquid phase k_f make it possible to predict the reaction rate constant in the solid state k_s. The corresponding experimental data can be conveniently represented in the form of the relation between the reciprocal of the rate constant and the correlation time of the rotational mobility $\tau_c = 1/\nu_c$. For the elementary reactions considered in this review, the above relation can be represented phenomenologically in the following form:

$$\frac{1}{k} = \frac{1}{k_f} + \alpha\tau_c, \qquad (4)$$

where α is an empirical coefficient and k_f the rate constant under the conditions of unlimited molecular mobility ($\tau_c \to 0$), i.e. in a non-viscous solution.

But it is precisely in the case of free radicals that the influence of molecular mobility on the kinetics of elementary chemical reactions can be conveniently investigated from the EPR spectra where one can simultaneously follow the kinetics of chemical reactions and the molecular mobility. The frequency of the motions of the radical which entered into the chemical reaction has been measured for reactions (2) and (3), so one can assume that the parameters τ_c characterise the molecular dynamics of the kinetic cage responsible for the occurrence within it of the elementary reaction (reactants + surrounding molecules of the medium). Fig.1 shows that the variation of the rate constant for reaction (2) can be satisfactorily expressed in a linear form in terms of the variables $1/k$ and τ_c. A similar relation has been observed also for reaction (3), where $1/k_f \simeq 0$, so that the dependence of k on ν_c is linear.

Evidently, the characteristics of the kinetics of the elementary chemical reactions examined above are due precisely to the specific features of the phase state of the polymer as a medium with limited molecular mobility. Such features are characteristic also of the elementary chemical reactions in solid matrices and viscous media.[19] It is therefore reasonable to find an analogous experimental approach to the study of the characteristic features of the kinetics of elementary biochemical processes, the most important of which is electron transfer.

The relation between the rate of a chemical reaction and rotational mobility has been investigated[20] for the model reaction

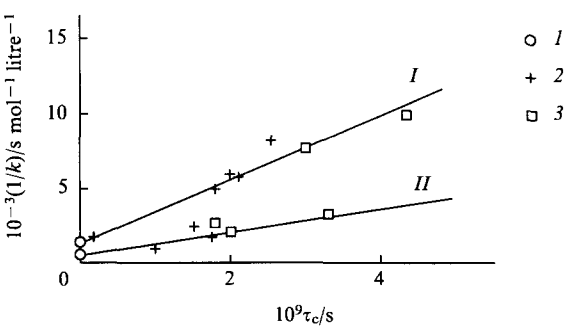
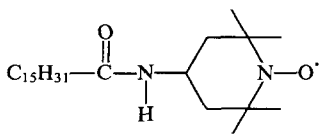


Figure 1. Experimental[7] dependence of the rate constants for the reaction of the nitroxyl radical with phenol on molecular mobility in terms of the variables of Eqn (4): (*1*) benzene; (*2*) polyethylene; (*3*) polypropylene; (*I*) 40 °C; (*II*) 50 °C.

involving the oxidation of the nitroxyl radical by tetranitromethane (TNM). The reaction was carried out in a homogeneous 3:1 water–*tert*-butyl alcohol mixture and in micellar systems based on non-ionogenic surfactants–Tritons X100 and WR1339, the viscous characteristics of which differ greatly. The micellar systems based on the Tritons involve a high degree of molecular organisation and can be regarded as simplified models of biological membranes. The nitroxyl radical



was used as the spin probe. The reaction kinetics were investigated simultaneously in terms of the intensity of the EPR spectrum of the radical.

The radical is used widely in the study of biological membranes and of liposomal and micellar systems. The long hydrophobic hydrocarbon chain of the radical enables it to be thoroughly incorporated in the micelles. In order to determine the location of the nitroxyl radical in the micellar solution, the dependence of the isotropic hyperfine interaction (HFI) constant for the nitrogen nucleus $2A_{iso}$ on the polarity of the medium was employed. It was found that the above quantity in micellar solutions is identical with the value in pure surfactants, which indicates that the radicals are located within the micelles.

The study of the rotational mobility of the nitroxyl radical showed that, on passing from aqueous alcoholic to micellar solutions of Tritons X100 and WR1339 at a constant temperature, the rotation correlation time τ_c increases sharply. It was found that the true rate constant, calculated taking into account the partition coefficient of tetranitromethane between the aqueous phase and the micelles, diminishes appreciably under these conditions. The reaction can be represented by the equations

$$\begin{aligned} R_2NO^{\cdot} + C(NO_2)_4 &\xrightarrow{k} R_2NO^+ + C(NO_2)_3^- + NO_2^{\cdot}, \\ R_2NO^{\cdot} + NO_2^{\cdot} &\xrightarrow{k'} R_2NO^+ + NO_2^-, \end{aligned} \qquad (5)$$

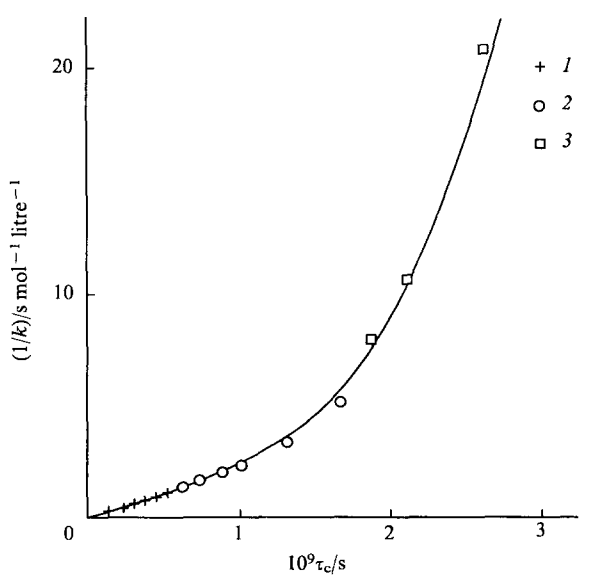


Figure 2. Dependence of the rate constant for reaction (5) on molecular mobility:[20] (*1*) 3:1 water–*tert*-butyl alcohol; (*2*) molecular solution of Triton X100; (*3*) WR1339.

where k is much smaller than k', so that the rate-limiting stage is electron transfer between the nitroxyl radical and the tetranitromethane molecule. Fig. 2 illustrates the dependence of $1/k$ on τ_c. Different values of τ_c at the same temperature are found for the aqueous alcoholic and micellar solutions. In the same medium, the quantity τ_c was varied by varying the temperature in the range 0–50 °C. The non-linearity of the plot in Fig. 2 can be attributed to the temperature dependence of the coefficient α in Eqn (4).

One should note specially that the transition from the homogeneous water–*tert*-butyl alcohol system to micellar systems with molecular organisation is manifested solely by a change in the reorientational mobility of the reactants. In other words, the reactivity is determined unambiguously by the molecular mobility, the measurement of which makes it possible to predict the rates of the elementary reactions even in complex systems such as micellar solutions.

III. The influence of the mobility of the medium on the kinetics of intramolecular radical substitution reactions

We examined above the correlation between the reaction kinetics and the molecular mobility of the reactants for bimolecular processes in which the characteristic reaction time exceeds by several orders of magnitude the characteristic time of rotation of the reactants. The influence of the mobility of the medium on the kinetics of slow bimolecular reactions appears comparatively evident in view of the high stereospecificity of these reactions and the need to assume a favourable mutual orientation of the reactants during the process. The kinetics of such reactions of free radicals have been investigated using the time variation of the intensity of the EPR spectra. The use under these conditions of stable nitroxyl radicals, for which a method of measurement of the rotational mobility correlation time has been well developed, makes it possible to find a relation between the reaction kinetics and the mobility of the medium. The effects associated with the modulation of anisotropic magnetic parameters (HFI constants and the g-factor), which lead to the broadening of the lines, are used to analyse the molecular mobility. In the region of rapid rotations of the radical ($\gamma b_{an}\tau_c \ll 1$, where b_{an} is the parameter of the anisotropy of the EPR spectrum and γ the gyromagnetic ratio for the electron), the line width, which depends on the molecular reorientations, is defined by the relation

$$\delta_m = d\gamma b_{an}^2 \tau_c , \qquad (6)$$

where $d \simeq 1$ is a coefficient. The parameter b_{an} includes the anisotropy of the g-factor and of the HFI constant:

$$b_{an} = H_0 \frac{\Delta g}{g} + \Delta B m , \qquad (7)$$

where H_0 is the external magnetic field, Δg the anisotropy of the g-factor, ΔB the anisotropy of the HFI constant, and m the overall projection of the nuclear spin. The components of the EPR spectrum of the radical with different values of m have different values of b_{an}, so that the degrees of broadening δ_m induced by the rotation of the radical differ for different components of the hyperfine structure.

In reality the observed line width Γ_m always includes also an intrinsic width δ_0 which is independent of molecular motions:

$$\Gamma_m = \delta_0 + \delta_m .$$

The contribution to line broadening due to rotation δ_m can be measured provided that $\delta_m > 0.1\delta_0$. The minimum measurable value of τ_c can then be defined thus:

$$\tau_c > 0.1 \frac{\delta}{\gamma d b_{an}^2} .$$

For stable nitroxyl radicals, the anisotropy parameters b_{an} are fairly large and can be measured in the usual 3 cm EPR range. This fact is apparently one of the main reasons for the widescale use of nitroxyl radicals in the study of molecular dynamics — in particular the relation between molecular dynamics and reactivity.

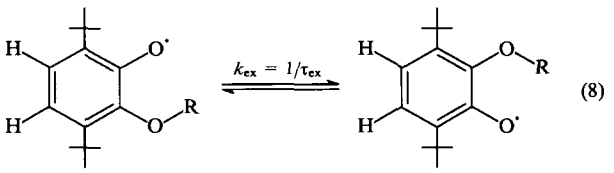
In order to discover this relation, it is essential to extend in experimental measurements the range of the measured rate constants for chemical reactions and to diversify the types of model objects. In particular, the elucidation of the reactivity of phenoxyl radicals in polymers is important in connection with the extensive application of substituted phenols as antioxidants.[21] For example, a purely qualitative correlation between the rate of reaction and the rotation frequency of the phenoxyl radicals in terms of the change in the line form of the EPR spectrum on passing from slow to fast motion has been observed[2] for reaction (1). For the PhO· radical, it is not possible to determine the quantity b_{an} from the EPR spectra in the 3 cm range and it is therefore not possible to obtain the values of τ_c and to compare them with the experimental rate constants, as has been done, for example, for reactions (2), (3), and (5) of nitroxyl radicals.

As 2 mm EPR spectroscopy developed, it became possible to measure the anisotropy parameters for a wide range of organic radicals, in particular, for radicals of the phenoxyl type.[22] This makes it possible to investigate the relation between molecular dynamics and the reactivity of such radicals. Furthermore, they constitute a unique class of free radicals entering into various chemical reactions, the elementary rate constants of which vary within a wide range as a function of the type of reaction and the structure of the radical.[23] In particular, rapid exchange processes, which, like rapid rotational motions of radicals, lead to dynamic effects in the EPR spectra, are characteristic of radicals of this type. However, in contrast to rotational processes, the effects of the chemical line broadening are based on the modulation of the isotropic magnetic parameters of the free radicals.[23] Such effects make it possible to obtain information about the kinetics and thermodynamics of rapid reversible chemical processes occurring with characteristic times $\tau = 1/k = 10^{-9}-10^{-6}$ s. The rotational mobility times τ_c in liquid viscous solutions fall within approximately the same range. This provides a unique possibility, where, by using simultaneously both types of dynamic effects in the EPR spectra of free radicals, one can obtain information under comparable conditions about the kinetics of the elementary chemical reaction and molecular mobility and the characteristic times τ and τ_c have comparable orders of magnitude.

The influence of the mobility of the medium on the kinetics of a series of intramolecular exchange reactions of phenoxyl or *o*-semiquinone radicals, which are intermolecular radical substitution reactions, was first demonstrated in a number of studies.[24-32] The methodological features associated with the corresponding EPR experiments will be examined in greater detail in relation to tin-containing substituted 2-R-oxyphenoxyl radicals. For other systems, we shall discuss only the kinetics of intramolecular reactions in viscous media.

1. EPR study of the molecular and chemical dynamics of free radicals in the 2 mm and 3 cm ranges

The 3,6-di-*tert*-butyl-2-R-oxyphenoxyl radicals were found to be convenient for the simultaneous investigation of the molecular and chemical dynamics of free radicals. A characteristic feature of these phenoxyl radicals is a degenerate tautomerism, which involves the reversible migration of the organoelement fragment R between two oxygen atoms and which constitutes an intramolecular radical substitution reaction.[33]



(8)

The rapid intramolecular migration of the fragment R at high temperatures leads to the equivalence of the two ring protons and a triplet EPR spectrum. At low temperatures, in the absence of chemical exchange the spectrum is represented by a doublet of doublets due to the two non-equivalent protons. In the intermediate temperature range, dynamic effects leading to the exchange broadening of the internal components of the quartet are observed. This makes it possible to find the rate constant or the characteristic time of the chemical exchange $k_{ex} = 1/\tau_{ex}$. We shall consider the possibilities of the EPR method for the simultaneous investigation of the molecular and chemical dynamics of radicals of the type indicated and shall analyse the relation between the quantities τ_{ex} and τ_c.

As noted above, for the calculation of the correlation times of the rotational mobility τ_c it is essential to know the parameters of the anisotropy of the radicals. In the original communications,[24-32] the measured values of τ_c for the radicals are quoted on the basis of rough estimates of the anisotropy parameters derived from poorly resolved 3 cm EPR spectra. The use of 2 mm spectroscopy for a more accurate measurement of the quantity τ_c is extremely important in the quantitative analysis of the influence of molecular mobility on chemical reactivity. The relation between τ_{ex} and τ_c has been investigated[34] with the aid of 2 mm EPR data for tin-containing 3,6-di-*tert*-butyl-2-R-oxyphenoxyl radicals, where R = $SnPh_3$ (**1**) or $SnClMe_2$ (**2**).

Fig. 3*a* presents the EPR spectra of frozen toluene solutions of radical **1** in the 3 cm and 2 mm ranges. Evidently in the former case it is impossible to obtain the anisotropy parameters, while in the latter the canonical components (g_x, g_y, g_z) of the *g*-tensor are manifested quite clearly. Furthermore, the corresponding component B_y of the HFI tensor is manifested in the *y*-orientation. Evidently, the doublet splitting is due to the interaction of the unpaired electron with the aromatic ring proton in the *para*-position relative to the non-coordinated oxygen atom, to which the highest spin density corresponds. The other two components of the HFI tensor (B_x and B_z) were estimated with the aid of computer modelling on the basis of the experimental line widths of the canonical components taking into account the fact that the isotropic HFI constant $a_H^{para} = (B_x + B_y + B_z)/3$ is known from the EPR spectra of the radical in solution. The anisotropy parameters found in this way for radical **1** are

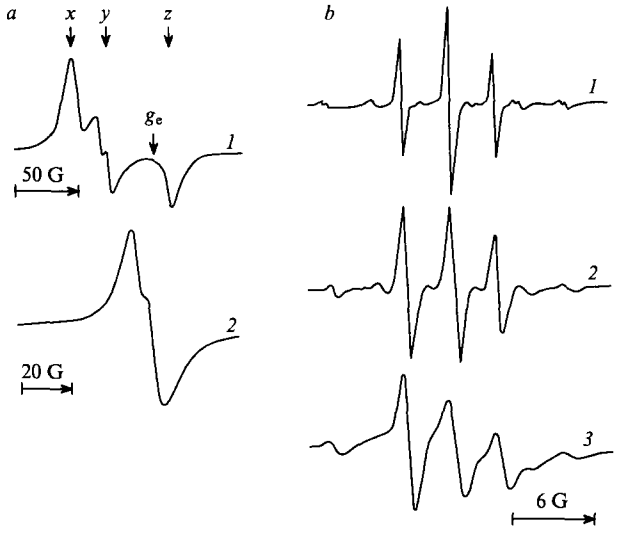


Figure 3. EPR spectra of radical **1**: (*a*) spectra of frozen toluene solutions of the radical in the 2 mm (curve *1*) and 3 cm (curve *2*) ranges; (*b*) spectra in the 3 cm range at 20 °C in the 1:2 (curve *1*) and 1:10 (curve *2*) hexane + liquid paraffin mixtures and in liquid paraffin (curve *3*); the satellite lines are due to the ^{117}Sn and ^{119}Sn isotopes.

as follows:

$$\Delta g_x = 1.88\times10^{-3},\ \Delta g_y = 0.44\times10^{-3},\ \Delta g_z = -2.32\times10^{-3},$$

$$\Delta B_x = 2.6,\ \Delta B_y = -2.6,\ \Delta B_z = 0.0\ \text{G}.$$

The contribution to the line width of the hyperfine structure component with an overall nuclear spin m can be represented in the form[35]

$$\delta_m = \frac{2}{15}\gamma\tau_c \sum_{i=x,y,z}\left(\frac{\Delta g_i H_0}{g} + \Delta B_i m\right)^2.$$

The overall line width for the hyperfine structure component is

$$\Gamma_m = \left(\frac{2}{3}\right)^{1/2}\left[\frac{2}{15}\gamma\tau_c \sum_{i=x,y,z}\left(\frac{\Delta g_i H_0}{g} + \Delta B_i m\right)^2\right] + \delta_0. \qquad (9)$$

It is assumed here that the lines of the hyperfine structure components have the Lorentzian shape and, since the line widths are measured between the points of maximum slope (the first derivative absorption line), it follows that $\Gamma_m = (2/3)^{1/2}(T_2)^{-1}$.

Fig. 3*b* illustrates the EPR spectra of radical **1** in media of different viscosity, which was varied with the aid of hexane – liquid paraffin mixtures having different component ratios. Under the conditions of rapid chemical exchange, the spectrum of this radical remains of the triplet type with a hyperfine structure constant $a = (1/2)\ (a_H^{para} + a_H^{meta})$, but an increase in the viscosity of the medium leads to a non-uniform broadening of the hyperfine structure components corresponding to the overall projection of the nuclear spin $m = -1, 0, +1$. We shall designate the widths of these components by Γ_{-1}, Γ_0, and Γ_{+1} respectively. Since the hyperfine structure constants for the protons in the *para*- and *meta*-positions in the aromatic ring of the radical are negative, the line width Γ_{-1} corresponds to the downfield component ($m = -1$). The following expressions for the line width of the hyperfine structure components can then be obtained from Eqn (9):

$$\Gamma_{-1} = \left(\frac{2}{3}\right)^{1/2}\left[\frac{2}{15}\gamma\tau_c \sum_{i=x,y,z}\left(\frac{\Delta g_i H}{g_0} - \Delta B_i\right)^2\right] + \delta_0,$$

$$\Gamma_0 = \left(\frac{2}{3}\right)^{1/2}\left[\frac{2}{15}\gamma\tau_c \sum_{i=x,y,z}\left(\frac{\Delta g_i H}{g_0}\right)^2\right] + \delta_0, \qquad (10)$$

$$\Gamma_{+1} = \left(\frac{2}{3}\right)^{1/2}\left[\frac{2}{15}\gamma\tau_c \sum_{i=x,y,z}\left(\frac{\Delta g_i H}{g_0} + \Delta B_i\right)^2\right] + \delta_0,$$

where δ_0 is the intrinsic line width and g_0 the isotropic g-factor of the radical.

Measurement of the line width showed that the central component with $m = 0$ is broadened to a much greater extent than predicted by Eqn (10). This is associated with the fact that the contribution to the broadening due to the inhibition of the intramolecular migration of the $SnPh_3$ group in radical **1** must be taken into account for this component. The contribution to the line broadening (only for the component with $m = 0$) due to chemical exchange is defined by the relation[35]

$$\delta_{ex} = \left(\frac{2}{3}\right)^{1/2}\gamma\tau_{ex}\left(\frac{\Delta a^2}{8}\right), \qquad (11)$$

where $\Delta a = a_H^{para} - a_H^{meta}$ is the difference between the hyperfine structure constants due to the protons in the *para*- and *meta*-positions, i.e.

$$\Gamma_0 = \left(\frac{2}{3}\right)^{1/2}\left[\frac{2}{15}\gamma\tau_c \sum_{i=x,y,z}\left(\frac{\Delta g_i H}{g_0}\right)^2\right] + \delta_0 + \delta_{ex}. \qquad (12)$$

The following expressions relating the line widths of the three components to τ_c and τ_{ex} can be obtained from Eqns (10)–(12) taking into account the anisotropies found for the magnetic parameters:

$$\Gamma_{+1} - \Gamma_{-1} = 1.47\gamma\tau_c,$$

$$\Gamma_0 - \Gamma_{-1} = 1.16\gamma\tau_c + 1.39\gamma\tau_{ex}. \qquad (13)$$

The numerical coefficients of τ_c and τ_{ex} have the dimensions G^2.

From the methodological point of view, the measurement of the line amplitude and not the line width is more convenient. The ratios of the integral intensities of the components with $m = -1, 0, +1$ are 1:2:1, i.e. $2I_{-1}\Gamma_{-1}^2 = I_0\Gamma_0^2 = 2I_{+1}\Gamma_{+1}^2$, where I_{-1}, I_0, and I_{+1} are the corresponding amplitudes. In this case, the line amplitudes I_{-1}, I_0, and I_{+1} and the widths of only the downfield component Γ_{-1} must be measured in order to calculate τ_c and τ_{ex}:

$$\left[\left(\frac{I_{-1}}{I_{+1}}\right)^{1/2} - 1\right]\Gamma_{-1} = 1.47\gamma\tau_c,$$

$$\left[\left(\frac{2I_{-1}}{I_0}\right)^{1/2} - 1\right]\Gamma_{-1} = 1.16\gamma\tau_c + 1.39\gamma\tau_{ex}. \qquad (14)$$

Fig. 4 presents the dependence of τ_{ex} on τ_c for radical **1**. The linear correlation $\tau_{ex} = \alpha\tau_c$ is retained, but the coefficient α, which is 3–4 according to the data of Rakhimov et al.,[28] is 0.5–1.0 according to more accurate estimates.[34]

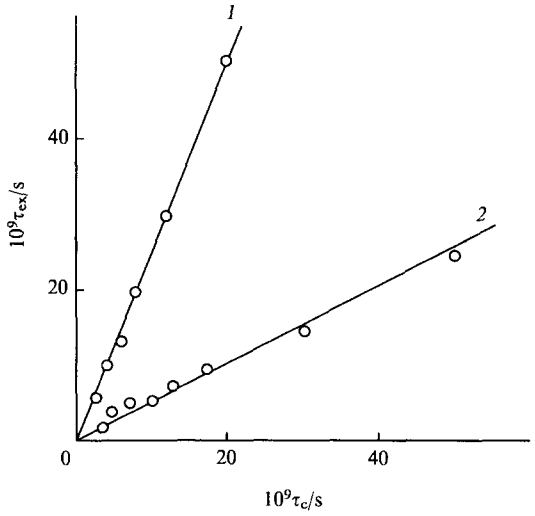


Figure 4. Dependence of τ_{ex} on τ_c for radical **1**: (*1*) according to data of Rakhimov et al.[28]; (*2*) calculation by Eqn (14) from EPR data in the 2 mm range[34] (τ_c was varied by raising the temperature from 0 to 50 °C in liquid paraffin).

The 2 mm EPR spectra of frozen solutions of radicals **1** and **2** are similar, but there is a somewhat different spectral pattern for radical **2**. Under comparable conditions (temperature, viscosity), the frequency of chemical exchange in radical **2** (intramolecular migration of the $SnClMe_2$ group) is smaller by 3–4 orders of magnitude than in radical **1**. As a result of this, the EPR spectra of radical **2** are quartets corresponding to slow and intermediate exchange conditions, where the two inner components of the quartet have undergone exchange broadening (Fig. 5*a*). An increase in the viscosity of the medium lowers the rate of chemical exchange (increases τ_{ex}). As for radical **1**, the extreme components of this spectrum are then non-uniformly broadened, which makes

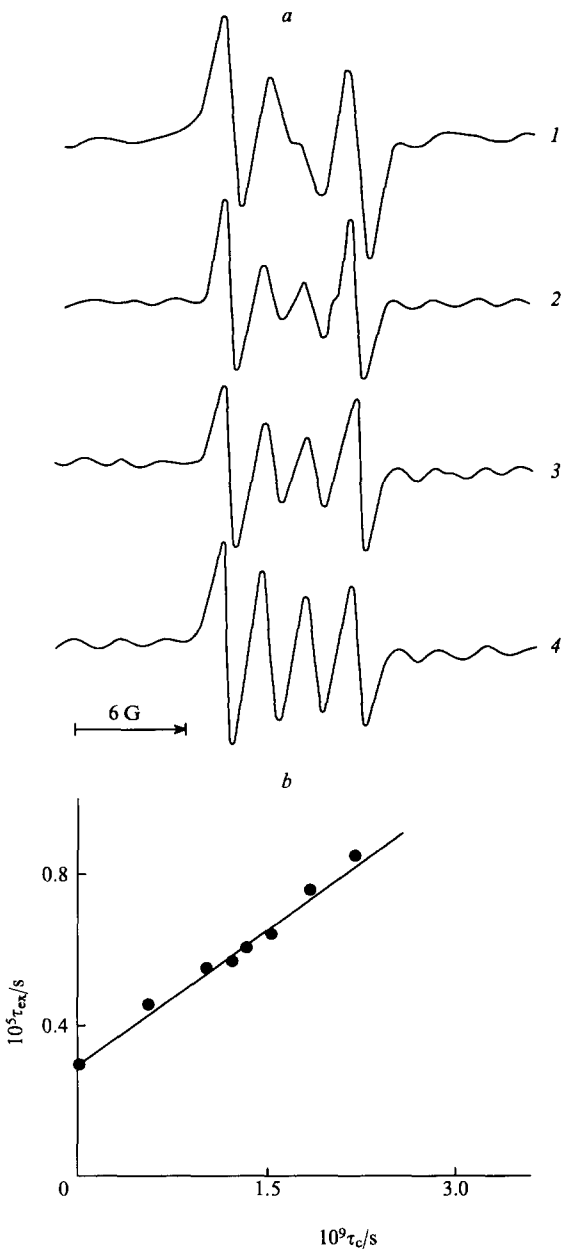


Figure 5. Spectroscopic characteristics of radical **2**: (*a*) EPR spectra in the 3 cm range at 30 °C in hexane (curve *1*), in the 1 : 1 hexane + liquid paraffin mixture (curve *2*), in the 1 : 10 hexane + liquid paraffin mixture (curve *3*), and in liquid paraffin (curve *4*); (*b*) dependence of τ_{ex} on τ_c obtained on varying the viscosity and temperature (from 20 to 30 °C).

it possible to estimate τ_c. The following experimental relation between τ_{ex} and τ_c has been obtained:[29]

$$\tau_{ex} = \tau_f + 8900\tau_c ,$$

where τ_f is the reaction time in a non-viscous medium ($\tau_c \to 0$). The times τ_{ex} and τ_c were found with the aid of the exact values of the anisotropy parameters for radical **2** (Fig. 5*b*). They are described by the relation

$$\tau_{ex} = \tau_f + 2400\tau_c .$$

The intramolecular radical substitution reaction (8) alters the directions of the magnetic axes in space (in particular the *y* axis of radicals **1** and **2** coincides with the axis passing through the C–O· bond involving the non-coordinated oxygen atom[22]). It is therefore impossible to rule out the possibility of the direct influence of chemical exchange on the effects of the modulation of the anisotropy parameters, leading to the broadening of the extreme components of the EPR spectra of radicals of the type considered (with $m = -1, +1$). In the case of radical **2**, the observed correlation between τ_{ex} and τ_c cannot be accounted for by the direct influence of chemical exchange on the measured τ_c, since the characteristic time of the exchange is three orders of magnitude greater than the characteristic time of molecular reorientations.

A completely different situation arises for radical **1**. As shown above, the characteristic times of the chemical exchange and the rotational motions for this radical are comparable ($\tau_{ex} \simeq \tau_c$), so that in the given instance it is necessary to consider the possibility of the direct influence of chemical exchange on the measured τ_c.

In order to elucidate the problem, a quantitative comparison was carried out[36] of the rotational mobilities of radical **1** and the corresponding isomeric radical 3,5-di-*tert*-butyl-2-triphenylstannyloxyphenoxyl **1A**.

Fig. 6 presents the EPR spectra of radicals **1** and **1A** under comparable conditions. In contrast to radical **1**, in radical **1A** there are no intramolecular migrations of the $SnPh_3$ group (because of the difference in the shielding of the oxygen atoms) and its EPR spectrum is a doublet due to the proton in the *meta*-position relative to the non-coordinated oxygen atoms. The non-uniform broadening of the components of the doublet is evidently caused solely by effects associated with the modulation of the anisotropic magnetic parameters of radical **1A** due to rotational motions. The anisotropic parameters of radical **1A** have been found[22] by 2 mm EPR. They make it possible to calculate the times τ_c for a radical in which there is no chemical exchange. The characteristic correlation time for the rotation of a radical without chemical exchange (i.e. radical **1A**) will be designated by τ'_c. Fig. 7 presents the rotation correlation times for radicals **1** (τ_c) and **1A** (τ'_c) under comparable conditions. It is essential to note in the first place that the dependence of τ_c on τ'_c is linear: $\tau_c = b\tau'_c$. This means that the linear relation between the characteristic time of the chemical exchange τ_{ex} and the 'true' correlation time of the molecular motions is observed in all cases for radical **1**. In liquid paraffin, in the temperature range from 15 to 50 °C, we have $b = 0.4$, whereas in toluene at appreciably lower temperatures (−100 to −75 °C) we have $b = 0.75$.

Thus the correlation time of the rotational mobility τ'_c of a radical without chemical exchange is greater than that of a radical with chemical exchange. This can be explained by the direct influence of the latter on the measured time τ_c for radical **1**, i.e. if one assumes that τ'_c is the 'true' correlation time of the rotational mobility of the radical, then the measured τ_c for the radical with chemical exchange is reduced compared with τ'_c. Predictably, at high temperatures, where the contribution of chemical exchange increases, the difference between τ_c and τ'_c increases.

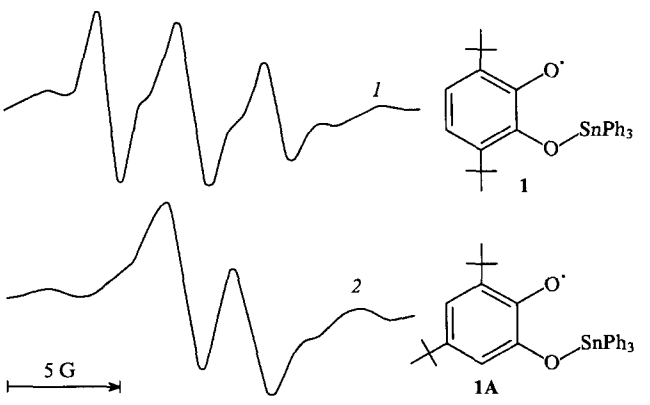


Figure 6. EPR spectra of radicals **1** (curve *1*) and **1A** (curve *2*) in liquid paraffin at 20 °C.

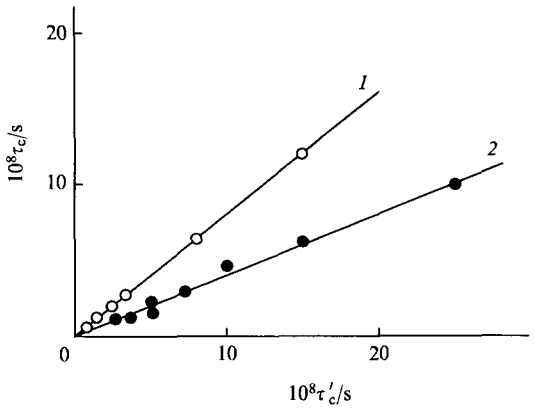
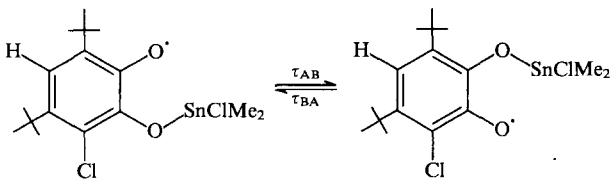


Figure 7. Correlation times of the rotational mobility for radicals **1** and **1A** in toluene for temperatures in the range −100 to −75 °C (line *1*) and in liquid paraffin for temperatures in the range 15 – 20 °C (line *2*).

The examples of the intramolecular reactions of radicals **1** and **2** examined represent chemical exchange between degenerate states (the forward and reverse reactions are identical). In substituted tin-containing oxyphenoxyl radicals with asymmetrically disposed substituents, one may observe reversible intramolecular processes which represent a non-degenerate tautomerism of the free radicals.[37] The influence of the mobility of the medium on the dynamics of the stannotropism of the 3,5-di-*tert*-butyl-2-chlorodimethylstannyloxyphenoxyl radical **3** has been investigated.[30] The chemical exchange process can be represented in this instance in the following form:



3A **3B**

The EPR spectrum of radical **3** in the absence of exchange at low temperatures constitutes a superposition of the spectra of two forms, **3A** and **3B**, differing in the constant for the hyperfine interaction with the aromatic ring proton. In the **A** form, the ring proton is in the *meta*-position relative to the non-coordinated oxygen atom with a_H^A = 2.3 G, whereas in the **B** form the ring proton is in the *para*-position with a_H^B = 4.9 G.[37] For high rates of exchange, an increase in temperature leads to the observation in the EPR spectra of dynamic effects due to transitions between the two forms of radical **3**. The equilibrium constant

$$K = \frac{I_B}{I_A} = \frac{k_{AB}}{k_{BA}} = \frac{\tau_{BA}}{\tau_{AB}}$$

can be determined from the ratio of the integral intensities, and analysis of the line broadening makes it possible to determine the chemical exchange frequency:

$$\nu_{ex} = k_{AB} + k_{BA} = \frac{\tau_{AB}\tau_{BA}}{\tau_{AB} + \tau_{BA}},$$

where $k_{AB} = 1/\tau_{AB}$ and $k_{BA} = 1/\tau_{BA}$ are the rate constants for the forward and reverse reactions respectively. Thus the rate constants for the forward and reverse reactions or the times τ_{AB} and τ_{BA} can be determined separately.

Similar dynamic effects are observed when the viscosity of the medium is varied: the exchange frequency diminishes on passing

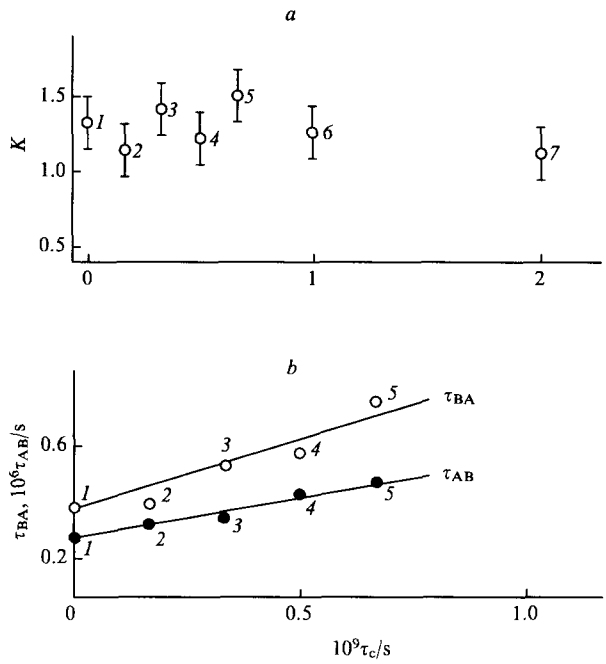


Figure 8. Dependence of the equilibrium constant (*a*) and the characteristic times for the forward (τ_{AB}) and reverse (τ_{BA}) reactions (*b*) on the correlation time of the rotational mobility τ_c at 15 °C: (*1*) hexane; (*2*)–(*6*) 1 : 1 (curve *2*), 1 : 3 (curve *3*), 1 : 5 (curve *4*), 1 : 7 (curve *5*), and 1 : 10 (curve *6*) hexane + liquid paraffin mixtures; (*7*) liquid paraffin; τ_{AB} and τ_{BA} were obtained under the conditions of intermediate exchange; since the spectrum at points *6* and *7* corresponded to slow exchange conditions, τ_{AB} and τ_{BA} were not calculated.

to more viscous media. The rotational mobility correlation time cannot be determined from the EPR spectra of radical **3** because the broadening induced by chemical exchange is much greater than the effects of the modulation of the anisotropic hyperfine interaction. For this reason, the values measured for radical **2** in the same media were adopted as the parameter τ_c. Fig. 8 presents the dependence of the equilibrium constant, τ_{AB}, and τ_{BA} on τ_c. Evidently, a nearly linear relation is observed between the chemical exchange times and the rotational mobility, while the equilibrium constant is independent of molecular mobility within the limits of the accuracy of the measurement.

2. Other intramolecular radical substitution reactions

The data presented above indicate a relation between molecular and chemical dynamics also for rapid reversible intramolecular reactions of free radicals. Eqn (4) also holds for such radicals and in the case of unimolecular reactions can be more conveniently expressed in the form

$$\tau = \tau_f + \alpha\tau_c, \qquad (15)$$

where $\tau = 1/k$ and $\tau_f = 1/k_f$.

The influence of molecular mobility on a series of intramolecular radical substitution reactions of type (8) involving other organoelement fragments R in 3,6-di-*tert*-butyl-2-R-oxyphenoxyl radicals, for example, R = ZnAcac (**4**), CdAcac (**5**), ZnS(S)CoBu (**6**), $PbPh_3$ (**7**), H (**8**) $\overset{+}{N}HBu^t_3$ (**9**), and $\overset{+}{N}H_2Bu_2$ (**10**), has been investigated in recent years. Since similar features of the EPR spectra in viscous media (under the conditions of rapid chemical exchange) are characteristic of radicals **4**–**10**, we shall discuss certain phenomenological characteristics of the relation between τ_{ex} and τ_c without going into the details of the EPR experiment.

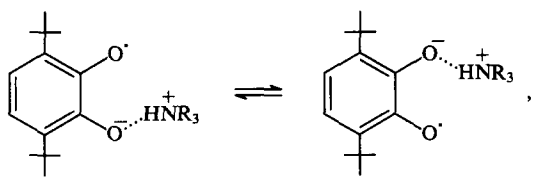
The study of the elementary reactions in condensed media can be usefully carried out within the framework of a formal-kinetic approach.[19] A characteristic feature of the temperature variations of the rate constants for reactions in condensed media, especially

reactions in the solid phase, is the deviation in certain cases from the Arrhenius relation

$$\ln k = \ln k_0 - \frac{E}{RT}. \quad (16)$$

Furthermore, this deviation is frequently 'masked', being manifested solely by anomalous values of the kinetic parameters—the pre-exponential factor k_0 and the activation energy E. The experimental values of $\ln k_0$ and E for isotypical reactions vary together under these conditions, i.e. the so called compensation effect is observed.[19]

The influence of the mobility of the medium on the kinetics of the intramolecular migration of a hydrogen atom in radical **8** and the kinetics of the migration of the hydrogen bond in the corresponding 3,6-di-*tert*-butyl-*o*-semiquinone radical-anion combined with alkylammonium cations,



where NR_3 = tri-*tert*-butylamine and di-*tert*-butylamine (radicals **9** and **10** respectively) has been investigated.[26]

The corresponding Arrhenius temperature dependences of the times τ_{ex} for media of different viscosity are represented by straight lines, i.e. the chemical reaction time τ_{ex} can be expressed in the form

$$\tau_{ex} = \tau_{ex}^0 \exp\left(\frac{E_{ex}}{RT}\right), \quad (17)$$

where $\tau_{ex}^0 = 1/k_0$ in conformity with Eqn (16) and E_{ex} is the activation energy for the reaction.

Table 1 presents the values of E_{ex} and τ_{ex}^0 for the migration of the hydrogen bond in radical **10** in media of different viscosity. Evidently, with increase in the viscosity of the medium, the quantity E_{ex} diminishes but τ_{ex}^0 increases. Furthermore, similar changes have been observed for a medium of the same composition when the temperature was reduced. Fig. 9 presents the dependence of $\ln \tau_{ex}^0$ on E_{ex}. The linearity of this relation indicates the existence of the compensation effect and the values of E_{ex} and τ_{ex}^0 have therefore no direct physical significance.

The observation of the compensation relation between E_{ex} and τ_{ex}^0 may indicate that the Arrhenius relation in the form of

Table 1. E_{ex} and τ_{ex}^0 for the migration of the hydrogen bond in radical **10** in different media.

Medium[a]	T/°C	E_{ex}/kcal mol^{-1}	τ_{ex}^0/s
LP	5–20	3.5	5.5×10^{-10}
H+LP (1:5)	−10–20	5.5	2.4×10^{-11}
H+LP (1:3)	−10–10	6.3	1.3×10^{-12}
H+LP (1:1)	−10–0	10.7	1.4×10^{-16}
H+LP (1:1)	−60 to −40	2.5	0.8×10^{-9}

[a] H = hexane, LP = liquid paraffin.

Eqn (16) or (17) does not in reality hold. This has been confirmed, in particular, by the temperature variation of τ_{ex} in terms of the Arrhenius variables (Fig. 10). Thus Eqn (17) cannot be used to estimate the elementary rate constants.

Evidently, the sharp change in the kinetic parameters of the reaction is associated with the sharp alteration of the state of the medium (phase or structural transition, etc.). Under these conditions, there is an abrupt change also in the nature of the motion of the radical, i.e. the parallel variation of τ_{ex} and τ_c with temperature is observed (Fig. 10). Consequently, the correlation between the molecular motions and reactivity exists both before and after the phase or structural transition. Despite the fact that the reaction considered is an extremely simple chemical process, occurring in a non-polar medium (hexane + liquid paraffin), the viscosity of the medium exerts a significant influence on its rate. Analysis of the relation between τ_{ex} and τ_c for radical **10** shows that τ_{ex} is approximately two orders of magnitude greater than τ_c. For the intramolecular hydrogen atom transfer reaction in radical **8**, a linear relation is also observed between τ_{ex} and τ_c, but these parameters are similar as regards order of magnitude, so that account must be taken of the possible direct influence of the migration of the hydrogen atom on the measured time τ_c.

A linear relation between τ_{ex} and τ_c for radical **10** is observed when both the temperature and the viscosity of the medium are varied, which can be accounted for by the weak temperature dependence of the coefficient α in Eqn (15). In certain cases, such a relation was observed for radicals of the type considered. As an example, we shall consider the data obtained for radical **7**.

Under conditions where $\tau_c = 0$ (the widths of the lines of the extreme components of the triplet EPR spectrum are identical), the ratios of the amplitudes of the components of the proton hyperfine structure are always 1 : 2 : 1. This means that $\tau_f = 0$, so that the coefficient represents the ratio of the chemical exchange time τ_{ex} and the rotational mobility correlation time τ_c.

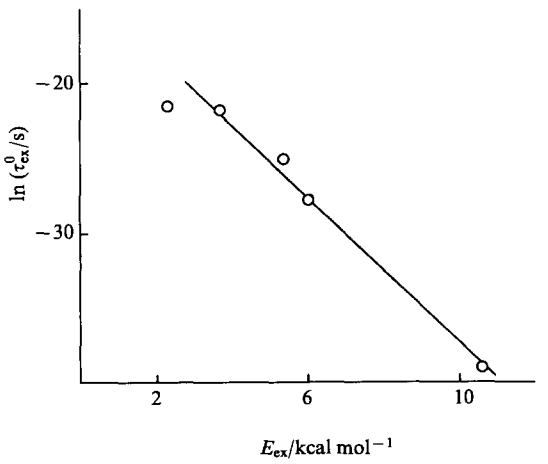


Figure 9. Dependence of $\ln \tau_{ex}^0$ on E_{ex} for radical **10**.

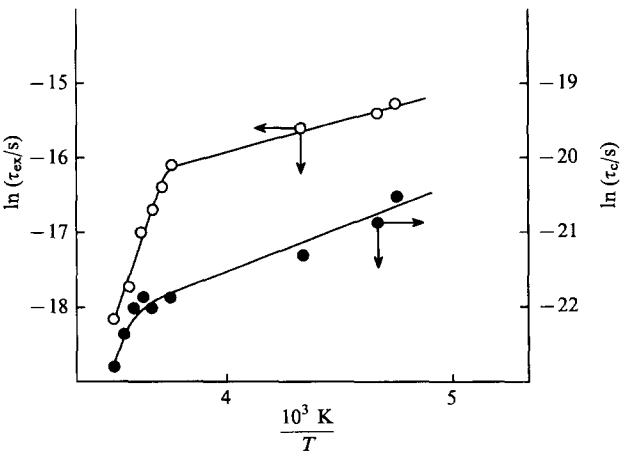


Figure 10. Temperature variation of τ_{ex} and τ_c in terms of the Arrhenius variables for radical **10** in the 1 : 1 hexane + liquid paraffin mixture.

Fig. 11 presents the EPR spectra of radical **7**. Evidently, a decrease in the rate of rotation of the radical leads to the inhibition of the chemical reaction both with increase in the viscosity of the medium and with decrease in temperature. However, comparison of spectra *4* and *5* shows that they correspond approximately to the same value of τ_c for the radical but at a low temperature (−134 °C, pentane) the central line is split, which corresponds to a slow chemical exchange. This means that, for the same value of τ_c, the inequality τ_{ex} (−134 °C) > τ_{ex} (20 °C) holds. This example indicates an increase in the coefficient α with decrease in temperature. Fig. 12 presents the relation between τ_{ex} and τ_c for radical **7**. The variation of τ_c with temperature and composition (viscosity) of the medium leads to a qualitatively different relation between τ_{ex} and τ_c. A satisfactory linear correlation between τ_{ex} and τ_c is observed only for the isothermal variation of the viscosity of the medium. If τ_c varies when the temperature is varied over a wide range, the relation between τ_{ex} and τ_c becomes non-linear and, as was to be expected, a decrease in temperature not only reduces the molecular mobility but also retards the chemical reaction proper, so that the relation between τ_{ex} and τ_c becomes steeper.

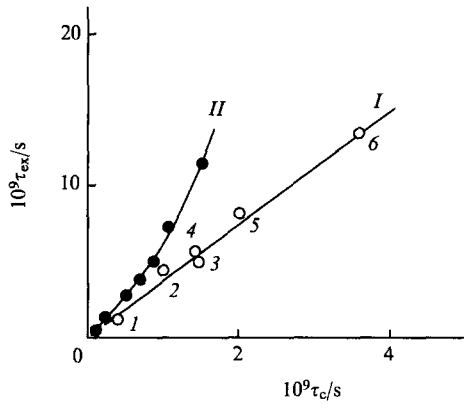


Figure 12. Dependence of τ_{ex} on τ_c for radical **7**: (*I*) variation of the composition of the medium at 20 °C with the aid of 1 : 1 (curve *1*), 1 : 3 (curve *2*), 1 : 5 (curve *3*), 1 : 7 (curve *4*), and 1 : 10 (curve *5*) heptane + liquid paraffin mixtures; (*6*) liquid paraffin; (*II*) variation of temperature in the range −85 to −20 °C in heptane.

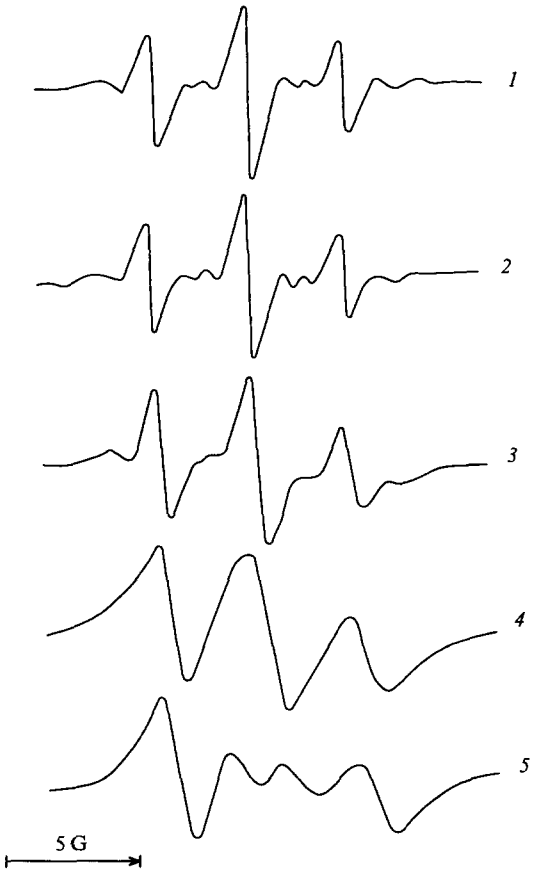
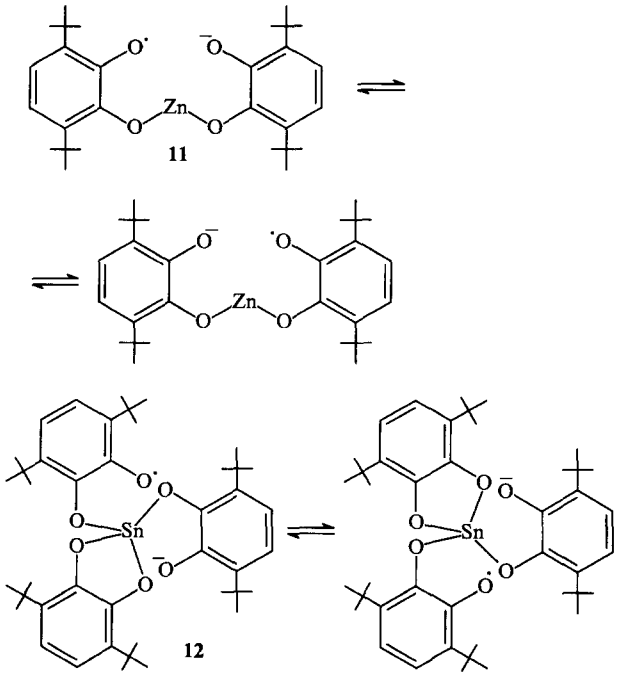


Figure 11. EPR spectra of radical **7** at 20 °C; heptane : liquid paraffin ratio in the heptane + liquid paraffin mixture: (*1*) 1 : 1; (*2*) 1 : 5; (*3*) 1 : 10; (*4*) liquid paraffin; (*5*) pentane at −134 °C; the satellite lines are due to the ^{207}Pb isotope.

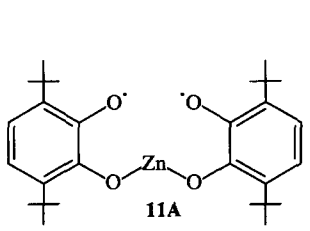
Hitherto we have considered the intramolecular radical substitution reactions in which the centre corresponding to the location of the unpaired electron changed as a result of the intramolecular transfer of an atom or group of atoms (exchange of the unpaired electron and of the bond within one ligand). Another type of intramolecular chemical exchange reactions may be observed for radical complexes of metals with two and three ligands between which the unpaired electron is exchanged (interligand exchange).

A similar interligand exchange of the unpaired electron (and charge) has been observed[38,39] by the EPR method in the radical-anion complexes of zinc and tin.

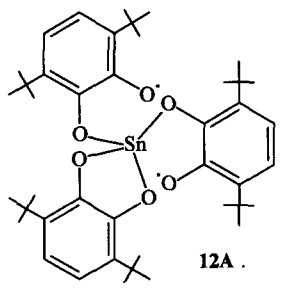


At low temperatures, the unpaired electron is located on one ligand, which leads to a triplet EPR spectrum determined by the hyperfine interaction with two equivalent protons (within one ligand, the unpaired electron either migrates rapidly between two oxygen atoms or is distributed symmetrically). At high temperatures, the unpaired electron migrates around all the ligands and the EPR spectra show splitting due to all the ligand protons (four protons in complex **11** and six protons in complex **12**). In the intermediate temperature range, the alternation of line widths is observed. Its analysis makes it possible to determine τ_{ex}. Specific line broadening, due to the effects of the modulation of the anisotropic magnetic parameters, has not been observed in the EPR spectra of the radical-anion complexes. This may be associated with the absence of an appreciable anisotropy of the

g-factor and the HFI constant. Therefore, the EPR spectra of the corresponding biradicals have been used[31] to determine τ_c:



11A



12A .

The EPR spectra of biradicals **11A** and **12A** in solution consist of broad singlet lines. In order to determine the rotation correlation time τ_c from the line width in the EPR spectra of the biradicals, the following formula must be used:[35]

$$T_2^{-1} = \frac{D^2}{20}\left(6\tau_c + \frac{10\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+\Delta\omega^2\tau_c^2}\right), \qquad (18)$$

where $D^2 = D_x^2 + D_y^2 + D_z^2$, D_x, D_y, and D_z being the principal values of the dipole–dipole interaction tensor in units of frequency. In our case, $\tau_c \simeq 10^{-9}$ s, so that $\omega\tau_c \gg 1$ and one need retain only the first term in Eqn (18). Having expressed D_x, D_y, and D_z in magnetic induction units, we obtain

$$\tau_c = \frac{5\delta H}{\sqrt{3}\gamma D^2},$$

where δH is the EPR line width of the biradical measured between points of maximum slope.

Fig. 13 presents the EPR spectra of the radical-anion complex **12** and the corresponding biradical **12A**. Evidently, with increase in rotational correlation time (with increase in the line width of the biradical in the EPR spectrum), the chemical exchange time τ_{ex} also increases (broadening of the components of the hyperfine structure with $m = \pm 2, \pm 1$). The relation between τ_{ex} and τ_c for the radical-anionic complexes **11** and **12** is described satisfactorily by Eqn (15). The times τ_{ex} and τ_c were measured in the temperature range -50 to 0 °C in solution in tetrahydrofuran (THF), the temperature variation of τ_{ex} and τ_c satisfying the Arrhenius relation. The kinetic parameters of the chemical exchange and of the rotational mobility for the radical-anionic complex **11** and biradical **11A** were found to be as follows: $E_{ex} = 4.5$ kcal mol^{-1}, $\tau_{ex}^0 = 3.9 \times 10^{-12}$ s, $E_c = 4.0$ kcal mol^{-1}, and $\tau_c^0 = 1.1 \times 10^{-13}$ s; for complexes **12** and **12A**, the corresponding parameters are $E_{ex} = 1.9$ kcal mol^{-1}, $\tau_{ex}^0 = 7.0 \times 10^{-10}$ s, $E_c = 4.6$ kcal mol^{-1}, and $\tau_c^0 = 2.5 \times 10^{-14}$ s (the accuracy of the determination of E_{ex} and E_c is to within 0.3 kcal mol^{-1}). We may note that the quantities E_c for biradicals **11A** and **12A** are actually identical, i.e. under comparable conditions τ_c (**11A**) = $b\tau_c$ (**12A**), where $b = 4$, which confirms the correlation between the rotation frequencies of probe radicals of different types in the same matrix. The quantities E_{ex} and E_c for radicals **11** and **11A** are similar and this is consistent with the observed relation between τ_{ex} and τ_c. For the radical-anionic complex **12**, the quantity E_{ex} is appreciably smaller than E_c, but τ_{ex}^0 is four orders of magnitude greater than τ_c^0. Here we are again dealing with the compensation effect, so that there is no point in discussing the absolute values of E and τ^0 but the correlation (15) nevertheless holds under these conditions.

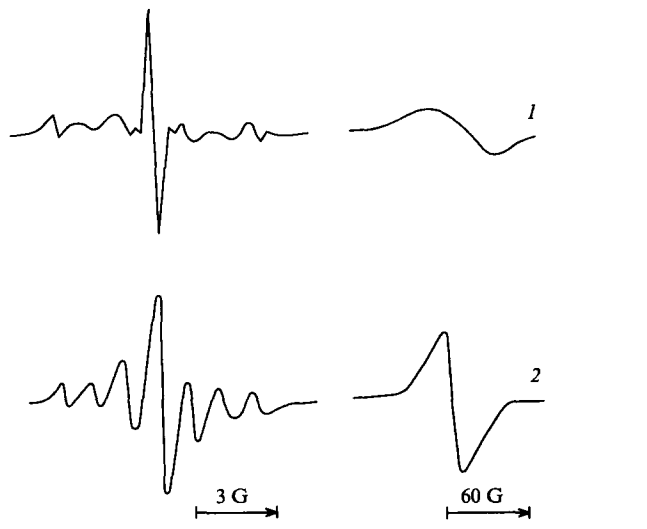


Figure 13. EPR spectra of complex **12** and the biradical **12A** in THF at different temperatures (°C): (*1*) −50; (*2*) 0.

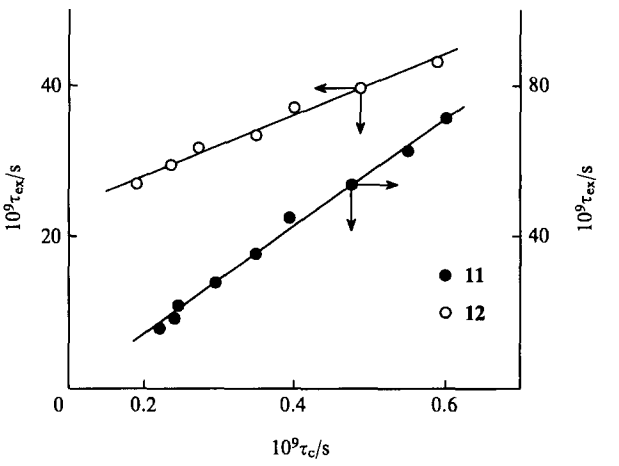
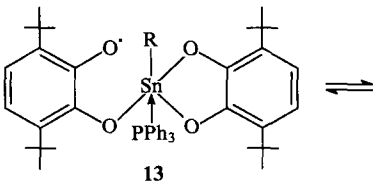
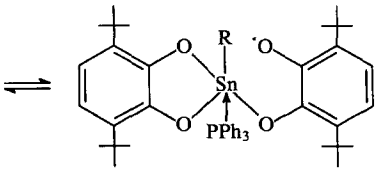


Figure 14. Correlation between τ_{ex} and τ_c for the radical-anionic complexes **11** and **12**.

Subsequently, it was possible to observe a relation between τ_{ex} and τ_c for interligand exchange under conditions where τ_c was varied by varying both the temperature and the viscosity of the medium. The correlation between the rotational mobility and the dynamics of the interligand exchange of the unpaired electron and the bond in radical **13** (R = 3,6-di-*tert*-butyl-2-R-oxyphenoxyl) has been investigated.[32]



13



It follows from the analysis of the EPR spectra of this radical that an increase in the viscosity of the medium leads to a broadening of the components with $m = -1$ and $+1$, i.e. the rate of the interligand exchange diminishes. This is also accompanied by a non-uniform broadening of the extreme

components of the hyperfine structure, which made it possible to estimate also τ_c for radical **13** at the same time. When τ_c is varied by varying the composition of the medium over a comparatively narrow temperature range (0–20 °C), τ_f and α are respectively 0 and 8. When τ_c is varied over a wide temperature range (−90 to 0 °C), the coefficient α becomes 25. Extrapolation of the corresponding straight line to $\tau_c = 0$ yields a negative value of τ_f, which means that the function of τ_{ex} in terms of τ_c is in fact non-linear in this case owing to the temperature dependence of α.

3. Molecular mobility and chemical reactivity. Interpretation of the experimental results

Table 2 presents the parameters of the phenomenological equation (15) for radicals **1**–**13**. For radicals **4**–**10** and **13**, the times τ_c were calculated on the assumption that the EPR spectra of frozen solutions of the radicals are axially symmetrical and that the parameters of the anisotropy are ~1 G, so that the parameters α for these radicals may differ according to the revised data for radicals **1** and **2**, but these differences do not exceed one order of magnitude.

Table 2. Parameters of Eqn (15) for intramolecular radical substitution reactions.

Radical	$10^9\tau_f$/s	α	T/°C	Medium	Ref.
1	0	0.5–1	0–50	LP	34
2	3000	2400	20–30	H + LP	34
3A	400	600	15	H + LP	30
3B	300	300	15	H + LP	30
4, 5	0	7–8	−90 to −10	Toluene	24
6	0.03	0.6–1	0–20	H + LP	24
7	0	4	20	Heptane + LP	27
8	0.8	1	20	H + LP	26
9	0	240	−60–20	H + LP	26
10	0	230	−60–20	H + LP	26
11	0	160	−50–0	THF	31
12	20	40	−50–0	THF	31
13	0	8	0–20	Toluene + LP	29
13	<0	25	−90–0	Toluene	29

Evidently, the phenomenological relation (4), found for the bimolecular reactions (2), (3) and (5) of nitroxyl radicals, may lead to Eqn (15) if the characteristic time of bimolecular reactions $\tau_r \sim 1/k$ is used as the kinetic parameter. The kinetics of these reactions were investigated by measuring the decrease in the intensity of the EPR spectra of the reacting radicals as a function of time under conditions where the initial concentration of free radicals was much lower than the concentration [M] of the molecules with which the free radicals reacted, so that the reaction occurred in a pseudo-unimolecular regime and its characteristic time was $\tau_r = \{k[\mathrm{M}]\}^{-1}$.

For the bimolecular reactions considered, the experimental rate constants k are in the range 10^{-4}–10 litre mol^{-1} s^{-1}, which is 10–15 orders of magnitude lower than the rate constants for diffusion-controlled reactions (10^{10}–10^{11} litre mol^{-1} s^{-1}). This actually means that the reaction proceeds in a radical–molecule contact pair R$^{\bullet}$...M surrounded by the molecules of the medium. The time τ_r can therefore be regarded as an analogue of τ_{ex} despite the fact that an electron or an atom is transferred between a radical and a molecule. A table of the parameters α and τ_f for bimolecular reactions was compiled on the basis of experimental data obtained for reactions (2), (3), and (5) (Table 3). The approximate relation[19]

$$\tau_{ex} = \frac{v^*}{k},$$

where v^* is the volume of the cage (usually ~5 litres mol^{-1}), was used.

Table 3. Parameters of Eqn (15) for bimolecular reactions.

Reaction	τ_f/s	α	T/°C	Medium	Ref.
(2)	10^3	10^{13}	40	Polypropylene (or polyethylene) + + benzene	7
(3)	$\ll 10^3$	10^5	28.5	Ditto	8
(5)	0	10^{10}	0–50	Water + *tert*-butyl alcohol (3 : 1)	20
(5)	0	$3\cdot10^{10}$	0–50	Triton X 100 (micellar solution)	20

Thus the EPR method is extremely effective in the study of the characteristic features of the kinetics of elementary reactions in viscous media. The results obtained hitherto have demonstrated convincingly the existence of a relation between molecular mobility (characterised by the time τ_c) and reactivity (characterised by the times τ_{ex} and τ_r) both for rapid intramolecular reversible reactions and for slow intermolecular irreversible chemical processes. In this connection, it becomes necessary to develop a general approach to an adequate explanation of Eqn (15) and an interpretation of experimental parameters of this relation.

Evidently, the classical theory of diffusion-controlled reactions as well as the transition state theory are unsuitable even for a qualitative explanation of the results. The existing models of the elementary chemical reactions in condensed media have been surveyed[19] and it was shown that some of them can be resorted to in order to account for the relation between the elementary rate constants for chemical reactions and the frequencies of molecular motions. One of such models is the Kramers model[14] in which the elementary chemical step is regarded as diffusional passage through the potential barrier in a viscous medium. The familiar expression for the chemical reaction rate constant, valid in a non-viscous medium, i.e.

$$\frac{1}{\tau_f} = \nu_0 \exp\left(-\frac{E}{RT}\right),$$

then assumes the following form for viscous solutions:

$$\frac{1}{\tau_r} = \frac{\beta}{\eta}\exp\left(-\frac{E}{RT}\right),$$

where η is the kinematic viscosity of the solvent and β is a parameter which depends on the frequency of the zero-point vibrations and the size of the reacting molecules.

Since $\tau_c \propto \eta$, the following expression can be obtained for the characteristic time of a chemical reaction:

$$\tau_r = b\tau_c \exp\left(\frac{E}{RT}\right).$$

Thus the Kramers model predicts qualitatively a linear correlation between τ_r (or τ_{ex}) and τ_c. The question arises to what extent this model is suitable for a quantitative (within the limits of an order of magnitude) interpretation of experimental results. Evidently, if $E = 0$, $\tau_r \simeq \tau_c$, and $b \simeq 1$ (in reality this coefficient can vary from 0.1 to 10), we have

$$\tau_r = \tau_c \exp\left(\frac{E}{RT}\right). \qquad (19)$$

In order to test this relation, use may be made of experimental results obtained, for example, for radical **2** (Fig. 5). The chemical line broadening effects for this radical are observed also in the limit of rapid molecular reorientations ($\tau_c \to 0$), so that $\tau_{ex} = \tau_f$ and it is possible to investigate the temperature variation of the chemical reaction time in the limit corresponding to the

unrestricted chemical mobility.[29] It was then found that the temperature variation of τ_f is described satisfactorily by the Arrhenius law:

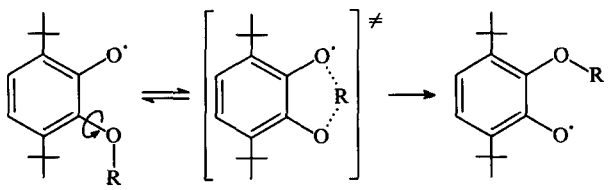
$$\tau_f = \tau_f^0 \exp\left(\frac{E_f}{RT}\right),$$

with $\tau_f^0 = 0.8 \times 10^{-13}$ s and $E_f^0 = E = 10.6$ kcal mol^{-1}. The normal value of the pre-exponential factor τ_f^0 permits the conclusion that the activation energy obtained is close to the true value.[19] Estimation of the ratio τ_{ex}/τ_c at 300 K by Eqn (19) yields $\sim 10^7$. However, it follows from the analysis of the spectroscopic characteristics that $\tau_{ex}/\tau_c \simeq 10^3 - 10^4$ (Fig. 5).

The Kramers model cannot explain also the insignificant difference between the rate constants for chemical reactions at different temperatures, which is reflected by the weak temperature dependence of the coefficient α (Table 2). This model also fails to explain the effect involving the levelling of reactivity observed for a series of bimolecular reactions in viscous media.[10]

A later theory of the electron transfer reactions in condensed media, developed by Marcus,[40] also includes the molecular mobility correlation time in the final expression for the rate constant, but this model deals only with electron transfer reactions in polar media, whereas the present review is concerned with purely homolytic processes in non-polar media. Nevertheless, one can adopt the principal idea of this theory, according to which a reorganisation of solvent molecules is essential for the occurrence of the elementary chemical step. This approach was used subsequently to devise a more general model of the indirect cage effect.[18] The principal idea underlying the model is that, even in the case of homolytic reactions in a non-polar medium, a change in the positions of the atoms and groups in the molecules surrounding the reactants is necessary for the formation of the transition state. Such molecular displacements can be characterised by the correlation time τ_c.

We shall assume that the elementary chemical reaction in a viscous medium proceeds via an intermediate metastable state which corresponds to the structure of the activated complex in a non-viscous medium (free space) but is attained via an additional energy barrier E_c associated with the necessity to reorganise the cages. For the intramolecular radical substitution reactions considered, this scheme can be represented in the form



$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* \xrightarrow{k_2} A,$$

where A* corresponds to a symmetrical disposition of the organoelement fragment R between two oxygen atoms. This structure of the radical arises as a consequence of the internal rotation about the C–O bond characterised by the barrier E_c. Evidently, the activation energy for the chemical reaction proper E_f corresponds to the barrier to the displacement of the fragment R between two oxygen atoms in the symmetrical structure, which must be overcome regardless of whether the radical is in a dense environment comprising the solvent molecules or in free space. In terms of the approximation of the method of stationary concentrations of A*, the following expression can be obtained for the rate constant:

$$\frac{1}{\tau_r} = k = k_2 \frac{k_1}{k_{-1}(1 + k_2/k_{-1})}.$$

The barrier E_c can be estimated, by a procedure similar to that used by Marcus,[40] as the height of the point of intersection of two parabolic curves. Then

$$E_c = \frac{(E_r + E_f)^2}{4E_r},$$

where E_r is the cage reorganisation energy.[18] Usually $E_f < E_r$ and one can therefore assume that

$$E_c \simeq \frac{E_r}{4} + \frac{E_f}{2}.$$

If $E_f \to 0$, the rate constant corresponds to the frequency of rotational motions, so that

$$\frac{1}{\tau_c} = \nu_0 \exp\left(\frac{E_r}{4RT}\right).$$

The rate constant for the chemical reaction in free space is given by

$$k_f = \frac{1}{\tau_f} = \nu_0 \exp\left(-\frac{E_f}{RT}\right),$$

where ν_0 is the universal pre-exponential factor.

The quantity

$$\frac{1}{\tau_{ex}} = \frac{k_f}{1 + (\nu_0 k_f)^{1/2}\tau_c} \tag{20}$$

or

$$\tau_{ex} = \tau_f + (\nu_0 \tau_f)^{1/2}\tau_c \tag{21}$$

may be found from the equations obtained above.[18] Eqn (21) corresponds exactly to the phenomenological Eqn (15), where

$$\alpha = (\nu_0 \tau_f)^{1/2} = \exp\left(\frac{E_f}{2RT}\right).$$

The model considered predicts, like the Kramers model, a non-linear relation between τ_{ex} and τ_c, but in the case of highly viscous media [i.e. for $\tau_c \gg (\tau_f/\nu_0)^{1/2}$] we obtain, in contrast to Eqn (19), the expression

$$\tau_{ex} = \tau_c \exp\left(\frac{E_f}{2RT}\right), \tag{22}$$

i.e. the model of the indirect cage effect explains the experimental values of τ_{ex}/τ_c, the levelling of reactivity, and the weak temperature dependence of the coefficient α. The energies E_f may be found from the experimental relations between τ_{ex} and τ_c under conditions where the temperature is varied over a wide range.[27, 28]

Thus, despite its approximate nature, the model of the 'reorganisation of the cage' examined above is satisfactorily consistent with the phenomenological relation (15). The experimental relations therefore make it possible to estimate chemical reactivity from molecular mobility data.

IV. Conformational transitions in free radicals. Relation between intramolecular mobility and the mobility of the medium

The rotational mobility correlation time τ_c is not the only parameter characterising molecular mobility. The molecular motions of radicals, leading to the averaging of the magnetic anisotropy, can differ from the motions responsible for the occurrence of the elementary chemical step. The measured quantity τ_c is evidently averaged over different types of motions of the spin probe (the motions around different molecular axes,

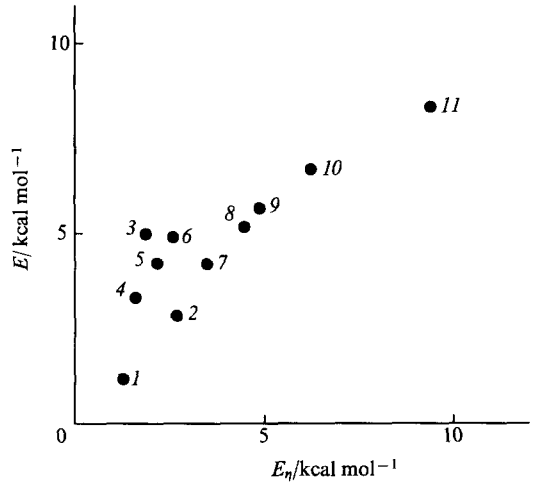


Figure 15. Relation between the activation energy for intramolecular rotations in radical **14** and the activation energy for the viscous flow of the solvent E_η (according to data of Jonkman and Kommandeur[42]): (*1*) carbon disulphide; (*2*) tetrachloroethylene; (*3*) mesitylene; (*4*) n-hexane; (*5*) n-octane; (*6*) n-decane; (*7*) ethanol; (*8*) 1-propanol; (*9*) 1-butanol; (*10*) 1-octanol; (*11*) cyclohexanol.

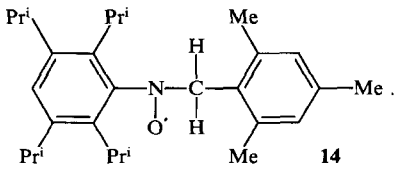
rotation of individual groups in the radical, molecular shifts responsible for the relaxation of the cage, etc.). A correction term must therefore be introduced into the expression for the coefficient α in Eqn (15):

$$\alpha = \alpha_0 \exp\left(\frac{E_f}{2RT}\right). \qquad (23)$$

The coefficient α_0 takes into account the correspondence between the molecular motions the average correlation time of which is measured experimentally and the motions leading to the occurrence of the reaction. For this reason, the parameter α_0 may be regarded as the ratio of the frequencies of the molecular motions along the reaction coordinate and the motions leading to the modulation of the anisotropic magnetic interactions of the probe radical. The necessity to take into account the coefficient α_0 in Eqns (4) and (15) makes it necessary to accumulate data on the molecular mobilities of the spin probes and on the relation between molecular motions of different types.

As a result of the development of 2 mm EPR spectroscopy, it has been possible to determine separately the characteristic frequencies of the rotation about different molecular axes for a series of nitroxyl radicals.[41] It was found that the ratio of the rotation correlation times depends only slightly on their absolute values, i.e. is independent of the viscosity of the medium.

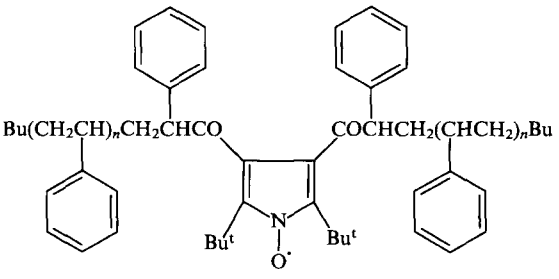
Analysis of the available literature data on intramolecular mobility or dynamics of conformational transitions has shown that these processes are also controlled by the molecular dynamics of the medium. As an example, one may consider a nitroxyl radical with the following structure:



14

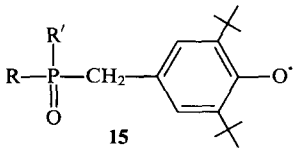
The EPR spectra of radical **14** indicate the intramolecular rotation of the benzyl group, which is manifested in the HFI modulation due to the two β-protons of this group.[42] Analysis of the line width led to the estimation of the kinetic parameters of the intramolecular rotation and it was shown that the activation energy for the intramolecular motion depends on the viscosity of the solvent. Fig. 15 presents the kinetic parameters of the intramolecular motions in radical **14** . Evidently, there exists a definite relation between the activation energies for the intramolecular motions and the solvent viscosity. The study of the dynamics of the reorientation motions of the spin probes in polymers has also shown that the activation energies for the rotation of radicals are close to the activation energy for segmental motions determined by the NMR method,[43, 44] but the rotation frequencies of the radicals are 2–3 orders of magnitude greater than the frequencies of the segmental motions. Thus a linear correlation of the type $\tau = \alpha\tau_c$, where $\alpha \sim 10^2 - 10^3$, also exists for these motions.

The dynamics of the conformational transitions in a spin-labelled molecule has been investigated[45] by the EPR method. It was found that the experimental results are described satisfactorily within the framework of the Kramers model.



In a study[46] of the relaxation-induced changes in the EPR spectra of a spin-labelled polyvinylpyridine, it was possible to characterise separately the motions of the macromolecule as a whole and the relative motions of the nitroxyl label, i.e. intramolecular motions. In the frequency range $10^8 - 10^9$ s^{-1}, these motions are characterised by the same activation energy, i.e. the mobility is determined in both cases by the solvent viscosity near the boundary of the macromolecule. In other words, the molecular mobility of the reactants (rotational, translational, conformational, etc.) is fully determined by the dynamic properties of the kinetic cage as a whole, including the molecules of the surrounding medium.

The examples considered above, indicating a relation between molecular motions of different types, were based on the parallel temperature variation of the frequencies of these motions. It has been shown[47] that the mobility of the medium exerts a direct influence on the dynamics of intramolecular rotational transitions in phosphorus-containing phenoxyl radicals having the following structure:



15

where R = R′ = Ph, R = Ph and R′ = EtO, or R = R′ = EtO.

The hyperfine interaction of the unpaired electron with the ^{31}P nucleus, the two equivalent protons of the CH_2 group in the *para*-substituent, and the two equivalent protons in the *meta*-positions in the aromatic ring is manifested in the EPR spectra of radicals **15** at high temperatures. As the temperature is reduced, the EPR spectra of radicals **15** exhibit a broadening of the central component of the triplet due to the protons of the CH_2 group of the *para*-substituent. At lower temperatures, these protons become non-equivalent. Such changes in the spectra are fully reversible as the temperature is varied, which indicates the occurrence of intramolecular processes in radical **15** owing to the

hindered rotation of the *para*-substituent around the C–C bond relative to the plane of the aromatic ring. In radicals of this type, the hyperfine interaction with the nuclei of the *para*-substituent takes place via a hyperconjugation mechanism[23] and the HFI constants are described by the relation

$$a = \rho_c^{\pi}(B_0 + B_2 \cos^2 \Theta) ,$$

where B_0 and B_2 are parameters which are respectively 0 and 43.5 G for the protons and 62 and 136 G for phosphorus,[48] $\rho_c^{\pi} = 0.4$ is the spin density in the *para*-position in the phenoxyl radical,[23] and Θ is the angle between the p orbital of the carbon atom in the *para*-position in the aromatic ring and the direction of the C–H or C–P bond. The difference between the HFI constants of the protons of the CH_2 group in the *para*-substituent at low temperatures is due to the difference between the angles Θ for these protons. Analysis of the line width makes it possible to find the characteristic time τ of the intramolecular transitions.

Fig. 16 presents the EPR spectra of radical **15** at the same temperature but in solutions of different viscosity (the viscosity was varied by adding liquid paraffin to toluene). Evidently, the increase in the viscosity of the medium entails a broadening of the central component of the triplets due to the protons of the CH_2 group, which indicates the inhibition of the intramolecular transitions. With increase in the viscosity of the medium, a non-uniform broadening of the components with a hyperfine structure, in particular the components due to the hyperfine interaction with the ^{31}P nucleus, also occurs. If one uses the anisotropic magnetic parameters of radical **15**, this makes it possible to determine the average rotational correlation time τ_c characterising the rotation of the radical as a whole.[47]

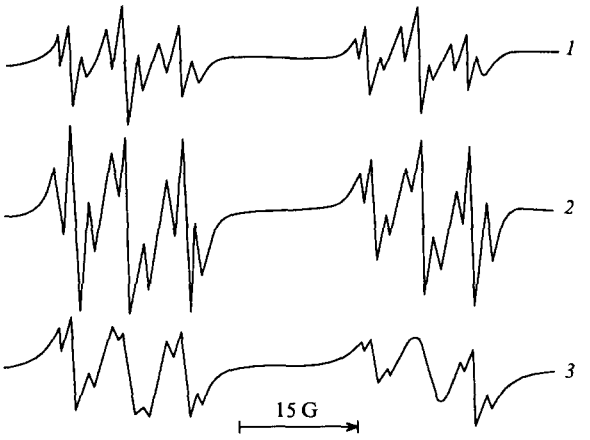


Figure 16. EPR spectra of radical **15** at 0 °C in different solvents: (*1*) toluene; (*2*) 1 : 3 toluene + liquid paraffin mixture; (*3*) 1 : 7 toluene + liquid paraffin mixture.

Fig. 17 presents the relation between τ and τ_c obtained on varying the composition of the medium and temperature. Evidently the experimental data are described satisfactorily by Eqn (15) for $\tau_f \ll \tau$. As the viscosity of the medium is varied, the coefficient $\alpha = 400$ remains constant under these conditions, while variation of the temperature over a wide range results in the variation of α in conformity with Eqn (23) ($\alpha_0 \simeq 30$, $E_f \simeq 2.8$ kcal mol^{-1}). The quantity α_0 is of the same order of magnitude as the parameters of the anisotropy of the rotational motions of nitroxyl radicals of complex shape obtained previously.

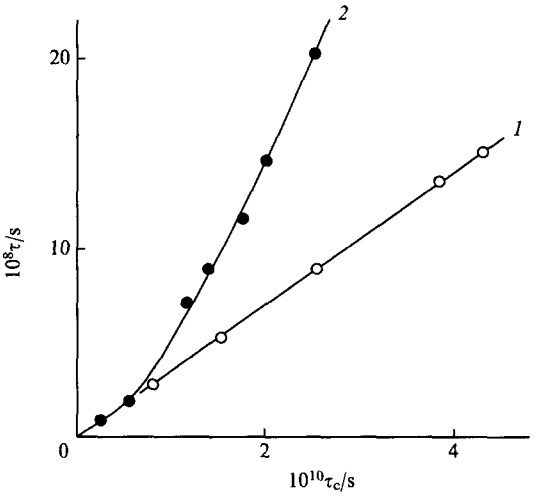
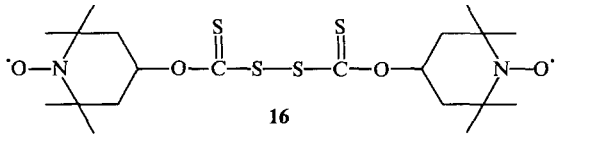


Figure 17. Dependence of τ on τ_c for radical **15**: (*1*) variation of the viscosity of the medium at 0 °C; (*2*) variation of temperature in toluene in the range from −70 to 20 °C.

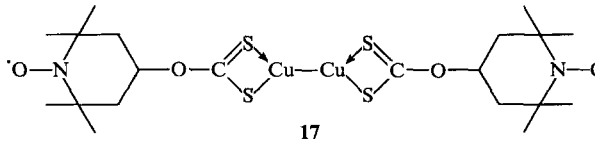
V. Relation between the rotational mobility and the dynamics of spin exchange in nitroxyl biradicals

Spin exchange can be regarded as a model of the electron transfer reaction, which is important in chemical and biochemical processes. The theory and methodological approaches to the study of spin exchange in nitroxyl biradicals have now been quite thoroughly developed.[49] Nitroxyl radicals and biradicals are the most convenient objects for the study of molecular mobility. We therefore regard it as evident that nitroxyl biradicals will also prove to be suitable objects whereby it will be possible to trace the relation between molecular and chemical dynamics — in the given instance the relation between molecular mobility and the dynamics of intramolecular spin exchange.

The influence of the mobility of the medium on the dynamics of spin exchange in biradicals based on a spin-labelled xanthate, having the structure

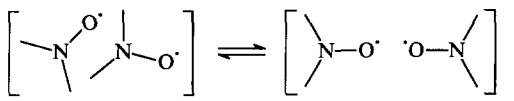


16



17

has been investigated.[50, 51] Biradicals **16** and **17** have quintet EPR spectra with alternately broadened biradical components.[52] They exist in solution in the form of at least three conformations: the 'extended conformation' with an exchange interaction constant $J = 0$ and two conformations with radical fragments in close proximity, for one of which $J = 0$ and for the other $J \gg a_N$, where a_N are HFI constants for the nitrogen nuclei. The mutual transitions between the conformations are described within the framework of the cage model.[49] According to the ideas of the 'cage' mechanism of exchange interactions in long-chain biradicals, the last two conformations are formed as a result of the mutual approach of the radical fragments, which enter a common 'cage' where they can interact. The elementary spin exchange step then occurs as a result of the direct collision of the radical fragments.



(24)

The alternation of the line widths of the biradical components of the EPR spectrum is caused by the changes in the conditions governing the modulation of the exchange integral within the cage.[49] Measurement of the line widths of the biradical components permits the calculation of the effective spin exchange time τ_{ex}:

$$\tau_{ex} = \frac{4(3)^{1/2}(\Delta H_2 - \Delta H_1)}{\gamma a_N^2}, \quad (25)$$

where ΔH_1 and ΔH_2 are the line widths of the first and second components of the EPR spectrum of the biradical measured between the points of maximum slope.

Since the EPR spectra of biradicals **16** and **17** constitute a superposition of the triplet and quintet spectra, the following formula must be used to determine τ_c for the radical fragments:[23]

$$\tau_c = 6.6 \times 10^{-10} \Delta H_1 \left[\left(\frac{I_1}{I_{1'}} \right)^{1/2} - 1 \right], \quad (26)$$

where I_1 and $I_{1'}$ are the amplitudes of the extreme components (downfield and upfield) of the EPR spectrum of the biradical. As will be shown below, $\tau_{ex} \gg \tau_c$ and the amplitudes of the biradical components and hence their widths remain unchanged. Therefore, in order to determine τ_{ex} one may use Eqn (25), neglecting at the same time the broadening of the biradical components associated with the effects due to the modulation of the anisotropic magnetic interactions by rotational motions.

Analysis of the EPR spectra of biradical **16** in media of different viscosity has shown (Fig. 18) that, with increase in τ_c, the biradical components become broadened and τ_{ex} also increases. The relation between τ_{ex} and τ_c for biradical **16** can be expressed in the form $\tau_{ex} = \alpha\tau_c$ and in the temperature range 0 to 60 °C the coefficient α remains unchanged. This permits the conclusion that the barrier to the activation of the spin exchange is low ($E_f < 2RT \simeq 1$ kcal mol^{-1}) and one can assume that $\alpha = \alpha_0$. For biradicals **16** and **17** in a hexane–liquid paraffin mixture, the parameter $\alpha_0 = 150-170$.[50] The comparatively high values of α_0 can be interpreted as follows: for 150–170 reorientation steps in the radical fragments there is only one spin exchange step, but the additional multiplier α_0 enters into the rate constant k_{ex} as a steric factor. In other words, the coefficient α_0 may be

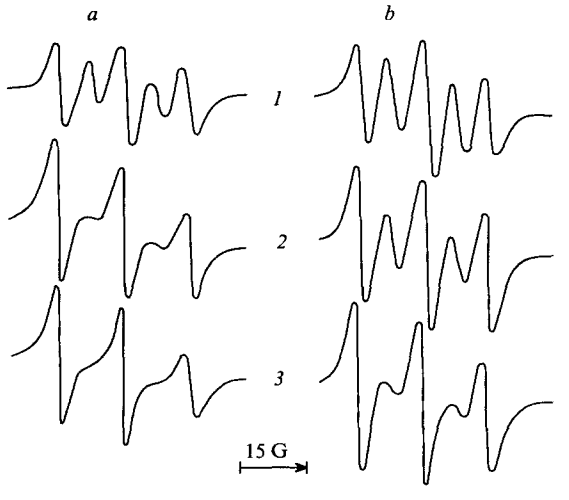


Figure 18. EPR spectra of biradical **16** at 20 °C (*a*) and 60 °C (*b*) in media with different viscosities: (*1*) 1 : 1 hexane + liquid paraffin mixture; (*2*) 1 : 10 hexane + liquid paraffin mixture; (*3*) liquid paraffin.

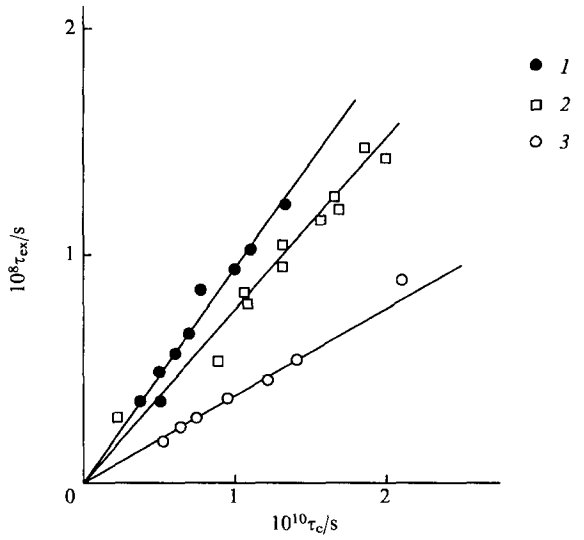


Figure 19. Dependence of τ_{ex} on τ_c for biradical **16** at variable temperatures in different solvents: (*1*) dimethyl sulfoxide; (*2*) 1-butanol; (*3*) THF.

interpreted as a parameter relating the frequencies of molecular motions of different types. For example, the rotation of radical fragments around the axis passing through the N–O bond does not lead to the collision of the radical fragments, as shown in Scheme (24).

The nature of the motion of the probe radicals may be influenced significantly by specific interactions with solvent molecules, so that, by analogy with the parameters of the anisotropy of the rotation of nitroxyl radicals,[41] one may expect changes in the parameters α_0 for biradicals **16** and **17** in different solvents. Fig. 19 illustrates the relation between τ_{ex} and τ_c for biradical **16** in different solvents (τ_c was varied by varying the temperature over a wide range). Evidently the linear correlation between τ_{ex} and τ_c holds satisfactorily, but the proportionality coefficient α_0 depends on the solvent. Table 4 presents the values of α_0 for different solvents together with the pre-exponential factors τ_c^0 and the activation energies E_c for the rotation of the radical fragment in the biradical. In all the solvents investigated, the temperature variation of τ_{ex} and τ_c is described satisfactorily by the Arrhenius relation. In conformity with the linear correlation obtained between τ_{ex} and τ_c, we find that

$$\tau_{ex}^0 = \alpha_0\tau_c^0 \quad \text{and} \quad E_{ex} = E_c .$$

Thus in a viscous medium the activation energy for intramolecular spin exchange in the biradical is identical with the barrier to the rotation of the radical fragment.

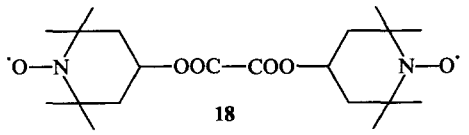
Evidently, the equality of the activation energies for different molecular processes frequently occurs in studies by the spin probe method. Some of these data were discussed above. Here one may

Table 4. The parameters α_0, E_c, and τ_c^0 for biradical **16** in different solvents.

Solvent	α_0	E_c/kcal mol^{-1}	τ_c^0/s	T/°C
Toluene	105±11	1.6±0.2	2.6×10^{-12}	−80 – 10
Acetone	100±10	2.2±0.4	7.7×10^{-13}	−60 to −5
DMF	85±8	4.5±1.0	3.4×10^{-14}	−30 – 60
DMSO	96±8	5.0±1.0	2.8×10^{-14}	10 – 80
Acetophenone	80±7	4.3±0.9	1.1×10^{-13}	30 – 90
Heptanol	75±15	7.9±1.0	1.1×10^{-15}	30 – 70
Butanol	78±9	3.3±0.5	6.8×10^{-13}	0 – 60
Methanol	50±7	3.7±0.5	1.1×10^{-13}	−50 – 10
THF	38±4	2.8±0.5	4.4×10^{-13}	−70 – 20

quote yet another example illustrating the relation between the dynamics of the intramolecular spin exchange and the rotational mobility.

The spin exchange in a biradical having the structure

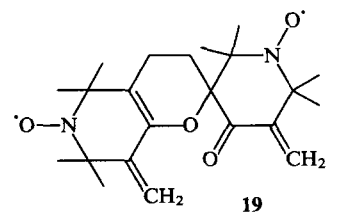


18

has been investigated[53, 54] by the double electron–electron resonance (DEER) method. The DEER method makes it possible to observe processes with lower frequencies than is possible when EPR is used. In the EPR spectra of biradical **18**, investigated in liquid paraffin at temperatures in the range −30 to +40 °C, hyperfine interaction with only one nitrogen nucleus is observed, i.e. intramolecular spin exchange is not observed on the EPR time scale. The DEER effect in biradical **18** is due to the intramolecular exchange interaction of the unpaired electron. The temperature variation of the frequency ν_{ex} of this interaction is described by the Arrhenius law with $\nu_{ex}^0 = 10^8\ s^{-1}$ and $E_{ex} = 3.5 \pm 0.7$ kcal mol^{-1}. The rotation frequency of the biradical ν_c, estimated from the EPR spectra as for the monoradical, is also described satisfactorily by the Arrhenius relation with $\nu_c^0 = 10^{11}\ s^{-1}$ and $E_c = 3.9 \pm 1.0$ kcal mol^{-1}. The values ν_{ex} measured for biradical **18** evidently correspond to the frequency of the rare collisions of radical fragments. The similarity of the activation energies for ν_{ex} and ν_c indicates a relation between the rotational and conformational motions of the biradical. Consequently, the relation $\tau_{ex} = \alpha_0\tau_c$, found previously for radicals **16** and **17**, also holds for biradical **18**. For biradical **18**, $\alpha_0 \simeq 1\,000$, which exceeds by an order of magnitude the corresponding values for radicals **16** and **17**.

As mentioned above, the spin exchange in flexible long-chain biradicals, to which biradicals **16**–**18** belong, takes place as a result of the collision between the nitroxyl fragments. Therefore the linear relation between the characteristic spin exchange time and the rotational mobility correlation time reflects the relation between the molecular motions of this type. The study of the relation between molecular mobility and the dynamics of spin exchange in nitroxyl biradicals, where the mutual approach and collision of the radical fragments is impossible and the spin exchange process takes place through the skeleton via an indirect mechanism, is of special interest. This type of spin exchange mechanism has been proposed for rigid nitroxyl biradicals.[49]

The influence of molecular mobility on the dynamics of spin exchange in a nitroxyl biradical having the structure



19

has been investigated.[55] The EPR spectra of biradical **19** have also been investigated.[56] In solutions with a low viscosity, the spectrum consists of a quintet with intensity ratios of 1 : 2 : 3 : 2 : 1 (if the spin had been localised on a single NO fragment, a 1 : 1 : 1 triplet would have been observed). The widths of the biradical components depended only slightly on temperature. This enabled the authors to conclude that an indirect mechanism of exchange via a chain of σ- and π-bonds operates.

The EPR spectra of biradical **19** in viscous solutions in liquid paraffin and in long-chain aliphatic alcohols have been investigated.[55] Fig. 20 shows that an isothermal increase in the viscosity of the medium entails an appreciable broadening of the biradical

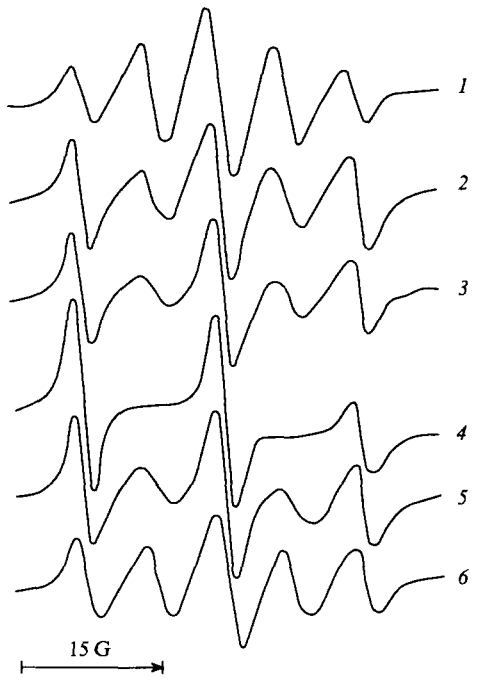


Figure 20. EPR spectra of biradical **19**: (*1*) in hexane at 20 °C; (*2*) in the 1 : 3 hexane + liquid paraffin mixture at 20 °C; (*3*) in the 1 : 5 hexane + liquid paraffin mixture at 20 °C; (*4*) in liquid paraffin at 20 °C; (*5*) in liquid paraffin at 40 °C; (*6*) in liquid paraffin at 60 °C.

components of the EPR spectra. A triplet is observed in the spectra in liquid paraffin, indicating the absence of intramolecular spin exchange on the EPR time scale. With increase in the temperature of the solution of biradical **19** in liquid paraffin, the appearance and subsequent narrowing of the biradical components are observed, which is clearly manifested by the increase in their relative amplitude. The ratios of the integral intensities of all the components of the spectrum always correspond to a binomial distribution. Similar changes are observed when the EPR spectra of biradical **19** in ethanol, butanol, octanol, and decanol are compared. The rate of intramolecular spin exchange falls in the series indicated.

Thus the inhibition of intramolecular spin exchange following a decrease in the mobility of the medium has also been observed for biradical **19**, although it is difficult to imagine what type of motion of the biradical may be responsible for the spin exchange process between the nitroxyl fragments. Despite the relatively rigid structure of biradical **19**, a definite rehybridisation of molecular orbitals, requiring relative shifts of the atoms in the molecule, is apparently necessary for the occurrence of the elementary spin exchange step. In this case, the relatively immobile species comprising the medium, forming 'the walls of the cage', hinder such displacements, which ultimately leads to the retardation of the intramolecular spin exchange. Thus a structural reorganisation of the cage (biradical + surrounding molecules of the medium) is necessary even for the occurrence of the very simple spin exchange step.

The relation between τ_{ex} and τ_c for biradical **19** is also linear (Fig. 21). In an inert medium, $\alpha_0 = 85$, whilst in an alcohol matrix $\alpha_0 = 200$. In solvents with a low viscosity (ethanol, hexane, toluene), the EPR spectrum of biradical **19** remains of the quintet type without appreciable broadening of the biradical components even at low temperatures (−60 to −80 °C), but the amplitudes of the extreme components of the spectrum also do not differ in this instance, which indicates a fairly rapid rotation of the biradical. This fact apparently reflects the characteristics of microscopic organisation of the cage around biradical **19**, since a monotonic decrease in the rotational mobility of nitroxyl fragments with

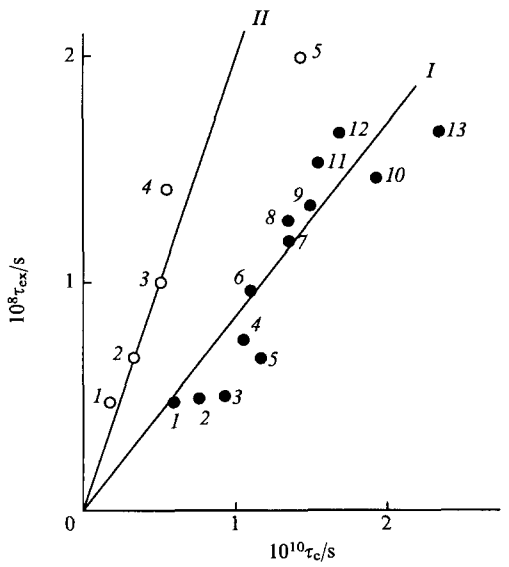


Figure 21. Dependence of τ_{ex} on τ_c for biradical **19**: (*I*) with variation of the composition of the medium (ratio of the concentrations of hexane and liquid paraffin) and temperature (°C): (*1*) 1 : 3, 60; (*2*) 1 : 3, 50; (*3*) 1 : 5, 60; (*4*) 1 : 3, 40; (*5*) 1 : 5, 50; (*6*) liquid paraffin, 60; (*7*) 1 : 5, 40; (*8*) 1 : 3, 30; (*9*) 1 : 5, 30; (*10*) liquid paraffin, 50; (*11*) 1 : 3, 20; (*12*) 1 : 5, 20; (*13*) liquid paraffin, 40. (*II*) In decanol at different temperatures (°C): (*1*) 60; (*2*) 50; (*3*) 40; (*4*) 30; (*5*) 20.

decrease in temperature is observed under these conditions for the 'usual' spin probes, for example, for biradicals **16** and **17**. By virtue of its structural characteristics in low-temperature solvents, biradical **19** can apparently ensure a molecular organisation of the immediate environment with a lower microscopic viscosity.

The data presented above indicate the need to consider the molecular dynamics of the kinetic cage as a whole, including the rotational mobility of the probe and the local motions of the medium. The stable perchlorotriphenylmethyl radical has been investigated[57] in the 2 mm EPR range. The absence of a hyperfine structure simplifies significantly the interpretation of the EPR spectra and the anisotropy of the *g*-factor is sufficient to obtain the necessary information both about the rotation of the spin probe and about the local motion of the medium. In this case, a linear relation was also observed between the characteristic time of the local displacements and the time of the reorientation of the probe molecule by large angles, which constitutes yet another example of the correlation between the frequencies of different processes in one matrix. One can imagine that the complex molecular motions in the condensed phase are effected as a result of the diffusional accumulation n of certain elementary 'quanta' of motion.[58] The frequencies of different types of motion then differ solely by the coefficient n^2 and are linearly correlated with one another. The local displacements of the medium, characterised by Grinberg et al.,[57] can play the role of such elementary motions, which constitutes the basis of the correlation between the frequencies of different molecular processes.

VI. Conclusion

The final aim of studies in the field of chemical physics is, in particular, the elucidation of the relation between the physical and chemical properties of molecules. In relation to chemical processes in condensed media, it is more correct to consider not the physical properties of individual molecules but the properties of the kinetic cage incorporating the reactants and the surrounding molecules of the medium which influence the reactivity. One of the main properties of such a cage is molecular mobility, the quantitative description of which permits the prediction of the difference between the reactivities in an ideal solution and in a real viscous medium of the type of glass, amorphous polymers, and biological structures.

The experimental results presented in this review give rise to the hope that the study of the molecular mobility of free radicals may provide a universal approach to the prediction of reactivity in viscous media and amorphous solids. The results of the investigation may be regarded as the starting point for the construction of microscopic models of chemical reactions in condensed media.

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