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Dynamics of Degenerate Tautomerism in Free Radicals

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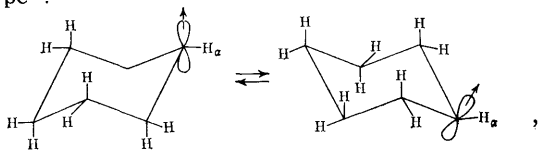
The theoretical principles of the application of the EPR method in the study of the kinetics of exchange processes involving free radicals and radical-anions are described and the results of studies by the EPR method of the tautomeric transformations in radicals and radical-anions, accompanied by the migration of atoms, cations, and organic and organoelemental fragments, are examined.
The bibliography includes 73 references.

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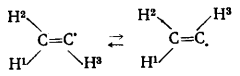
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I. INTRODUCTION

In the present review an attempt is made to survey the results of kinetic studies by the EPR method of tautomeric transformations in free radicals and radical-anions or more precisely the reversible intramolecular migrations of atoms and organic or organoelemental fragments between equivalent (or almost equivalent) positions in the molecule and of the cations in pairs formed with radical-anions. Such migration is accompanied by a synchronous redistribution of the unpaired electron density, which leads to a change in the EPR spectra of the species investigated. The application of the EPR method to the study of phenomena of this kind is based on the analysis of the line width in the hyperfine structure (HFS) of the EPR spectra, which frequently proves to be extremely sensitive to changes in the rates of tautomeric transitions. When applied to such processes, the EPR method provides unique possibilities for the investigation of the kinetics of many rapid transitions, the characteristic times of which are in the range between 10^{-6} and 10^{-10} s. There are several types of effects leading to a change in line width, but, for the problems discussed in this review, the most valuable information can be obtained by analysing the so called alternation of line widths in EPR spectra. This effect was observed in 1962 by Bolton and Carrington [1] and independently by Freed and Fraenkel [2]. In the Soviet Union, one of the first investigators to understand this phenomenon was V.V.Voevodskii, under whose supervision research was carried out at the beginning of the 1960s on the inversion isomerisation of the cyclohexyl radical of the chair–chair type [3]:



the *cis–trans* isomerisation of the vinyl radical [4]:



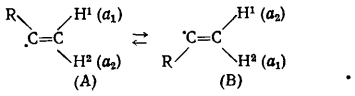
and the delocalisation of the unpaired electron in bridged radical-anions [5] $[Ar-X-Ar]^{-}M^{+}$. By analysing the alternation of line widths, it is possible to obtain extremely valuable information about the kinetics of various processes with participation of paramagnetic species. During recent years the method of analysis of line widths in EPR spectra has been closely applied in the study of processes such as the isomerisation of radicals, conformational transitions, electron and proton exchange reactions, and the tautomerism of free radicals and radical-ions.

Before discussing the results of these studies, we shall consider briefly the theoretical principles of the application of the EPR method to the study of the kinetics of exchange processes involving free radicals.

II. THEORETICAL PRINCIPLES

1. Qualitative Considerations

The alternation of line widths in EPR spectra is interpreted on the hypothesis that the hyperfine interaction (HFI), caused by some intermolecular or intramolecular processes, is modulated. We shall consider initially the simplest case where the radical contains only two nuclei with a spin $I = 1/2$. As an example we shall consider the vinyl radical:



Suppose that the HFI constant $a_2 > a_1$. If the radical does not isomerise or the rate of isomerisation is very low, the EPR spectrum corresponds to the picture presented in Fig. 1*a*, where the positions of lines relative to the centre of the spectrum and the spin states of the protons H^1 and H^2 are represented in a conventional manner.

We shall examine the change in the spectrum with increase of the rate of mutual transitions between forms (A) and (B). At first sight, it may appear that both forms of the radicals are identical and therefore there should be no change in the spectrum on transition from one form to the other. However, when account is taken of the spin state of the protons, this is not found to be the case. On passing from form (A) to form (B), the constants a_1 and a_2, corresponding to HFI with the H^1 and H^2 protons in the initial form, correspond in form (B) to HFI with the H^2 and

H^1 protons or, in other words, the protons as it were change places. If the constants a_1 and a_2 in the expressions $\pm\frac{1}{2}(a_2 \pm a_1)$, which characterise the positions of the lines in the spectrum, are made to change places, then it is readily seen that the extreme lines remain in the same positions, while the inner, central components change places or frequency exchange is said to take place. From this very simple picture follows a very important rule, according to which only lines corresponding to identical overall projections $[M_I(H^1) + M_I(H^2)]$ of proton spins undergo frequency exchange.

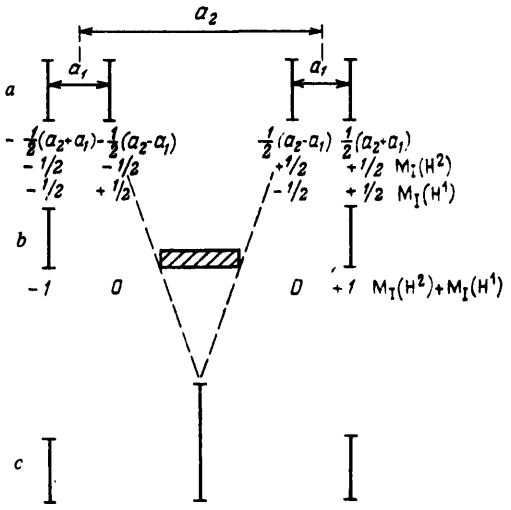
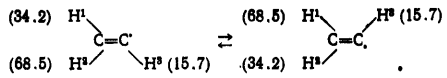


Figure 1. Schematic illustration of the EPR spectrum of an R-substituted vinyl radical: *a*) slow exchange; *b*) intermediate exchange; *c*) fast exchange.

If the rate of isomerisation is not too high, such frequency exchange leads to the broadening and merging of the central components, which is indicated in Fig. 1*b* by the shaded rectangle. In the limiting case of rapid exchange so-called exchange narrowing takes place and the spectrum consists of a triplet with intensity ratios of 1 : 2 : 1 (Fig. 1*c*). A necessary condition for the above picture of the changes in the EPR spectrum as a function of the frequency of the isomeric transition to be valid is antiparallel changes in the two HFI constants a_1 and a_2, i.e. it is necessary that they should be anticorrelated. Indeed this condition holds for the given radicals. While HFI with the H^1 proton becomes more intense, that with the H^2 proton is weakened. As we shall see subsequently, this situation is very frequently encountered in practice.

On the basis of the behaviour of the EPR lines, analysed above, in the spectrum of an R-substituted vinyl radical, it is easy to understand the variations in the EPR spectrum of the unsubstituted vinyl radical under different conditions in the recording of the spectrum. If the radical is obtained at 77 K by the reaction of a hydrogen atom with acetylene[4], an eight-line spectrum (illustrated in Fig. 2*a*) is observed, in agreement with the hypothesis that there are three non-equivalent HFI constants: $a_2 = 68.5$ G, $a_1 = 34.2$ G, and $a_3 = 15.7$ G.



If the same radical is obtained in the liquid phase[6], then the spectrum shows only four lines corresponding to the extreme lines of the low-temperature spectrum. Such transformation of the spectrum can be understood if it is assumed that the two isomeric forms of the radical are involved in rapid interconversion in solution, which leads to the antiparallel modulation of the HFI constants for the H^1 and H^2 protons. For the radicals where the orientations of the nuclear spins of the H^1 and H^2 protons are the same ($\alpha_1\alpha_2$ or $\beta_1\beta_2$), the transition from one tautomeric form to another does not entail a line shift, and for this reason the extreme lines remain narrow. The lines corresponding to the $\alpha_1\beta_2$ or $\beta_1\alpha_2$ state will be displaced and, for a certain rate of transformation, may become broadened to such an extent that they cannot be observed at all (Fig. 2*b*).

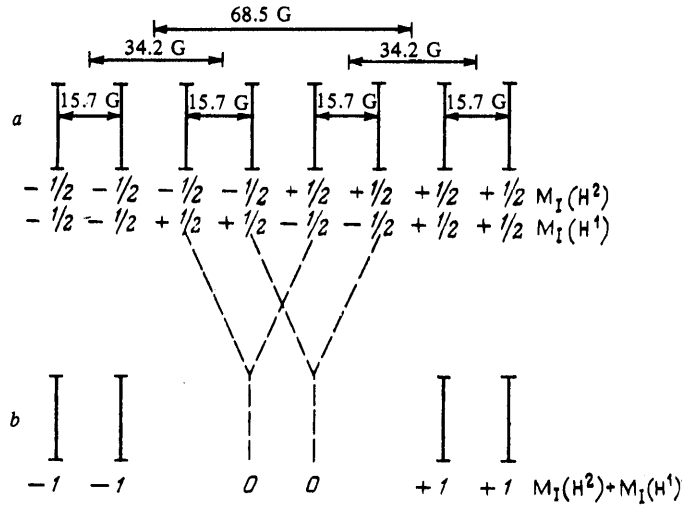


Figure 2. The influence of the rapid interconversion of the tautomeric forms of the vinyl radical on the EPR spectra at 77 K: *a*) spectrum of the radical in a rigid matrix; *b*) spectrum of the radical in the liquid phase.

2. Relation Between Line Width and Kinetics of the Exchange

The graphical description of the broadening of certain components of the EPR spectrum discussed above provides a clear qualitative picture of the influence of transitions between tautomeric forms of the radical on the spectrum. The quantitative relation between the broadening of the components and the frequencies of the intramolecular transformations, on the basis of which it is possible to obtain detailed kinetic information, is examined below.

It is possible to distinguish two main types of effects determining line width: effects associated with the lifetime of the given spin state and effects leading to the fluctuation of the energies of these states. Effects of the first type are determined by the characteristic spin–lattice relaxation time T_1 and those of the second type are determined by the spin–spin relaxation time T_2'. In chemical applications it is reasonable to restrict the treatment to the line widths determined by the reciprocal of the time T_2, which is related to T_1 and T_2' as follows:

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2T_1}. \qquad (1)$$

The main task of the theory is to find a quantitative relation between line width $(1/T_2)$ and the kinetic parameters of radical exchange reaction. There are two fundamental approaches to this problem. According to the first, the changes in line width as a result of chemical exchange processes can be described with the aid of modified Bloch equations[7,8], which make it possible to describe the spectra over a wide range of exchange frequencies—from the fully averaged spectrum to the spectrum corresponding to two individual forms of the radical. The second approach, based on the analysis of the relaxation matrix[9], yields a satisfactory agreement with experiment only at high frequencies. We shall consider further the main corollaries arising from the solution of the modified Bloch equations, which are necessary for the interpretation of the experimental data.

The physical significance of the broadening of the lines in EPR spectra is that the reciprocal transitions of the radical from one form to the other alter the local fields in which the unpaired electron is located, which entails a shortening of T_2 and a broadening of the corresponding lines.

Consider a free radical which may exist in two different forms A and B to which correspond different EPR spectra. We shall assume for simplicity that the concentrations of the two forms are identical and that only one EPR line corresponds to each. If there is exchange between forms A and B in this system, the spectrum will depend significantly on the rate of the exchange process, or, in other words, on the lifetimes of forms A and B. The theory usually involves the time τ which is related to the average lifetimes τ_A and τ_B in the following manner:

$$\tau = \tau_A\tau_B/(\tau_A + \tau_B). \qquad (2)$$

It is seen from this expression that, when $\tau_A = \tau_B$, the average lifetime of each form, A or B, is 2τ. It is usual to divide exchange processes into three main types depending on their rates: slow exchange, rapid exchange, and intermediate exchange. We shall consider the theoretical form of the spectrum for each specific case.

(a) Slow exchange. If the rate of interconversion of forms A and B is low, then τ is large compared with the difference between the resonance frequencies $(\omega_A - \omega_B)$, and the spectrum consists of two individual signals with an intrinsic width $1/T_{2,0}$ (Fig. 3*a*). With increase of the rate of interconversion, both components are broadened, the broadening in the case of slow exchange being related to the lifetime τ in the following manner:

$$\Delta(1/T_2) = 1/2\tau\gamma_e, \qquad (3)$$

where γ_e is the gyromagnetic ratio for the electron.

(b) Rapid exchange. With increase of the exchange frequency, the lines are displaced towards the centre of the spectrum and merge into a single exchange-narrowed line (Fig. 3*d*), whereupon the frequency of chemical exchange becomes much greater than the frequency difference $(\omega_A - \omega_B)$, i.e. $\frac{1}{2}\tau \gg (\omega_A - \omega_B)$. For very rapid interconversions, the line broadening is given by the following expression[10]:

$$\Delta(1/T_2) = (\omega_A - \omega_B)^2\tau/4 = \gamma_e(H_A - H_B)^2\tau/4, \qquad (4)$$

where H_A and H_B are the resonance values of the magnetic field for forms A and B. When the rate of interconversion of forms A and B reaches the upper limit, the central line is again narrowed to its intrinsic width $1/T_{2,0}$ (Fig. 3*e*).

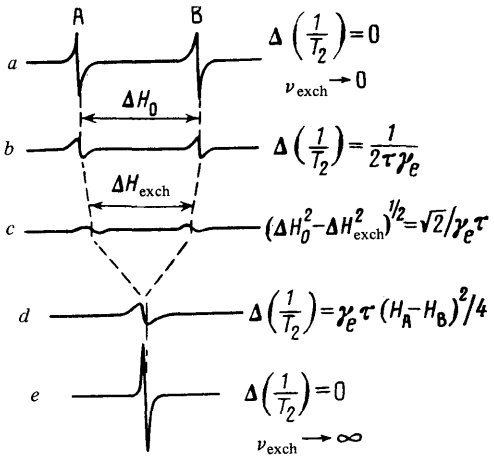


Figure 3. Schematic illustration of the influence of the rate of interconversion of the A- and B-forms of the radical on the EPR spectrum.

If the probabilities of the formation of each form of the radical involved in the exchange are P_A and P_B, the lines are displaced towards a weighted-mean position:

$$\langle H\rangle = (P_AH_A + P_BH_B)/(P_A + P_B). \qquad (5)$$

This situation is reflected in Figs. 3*c* and 3*d*. The line broadening is in this case expressed by the relation[10]

$$\Delta(1/T_2) = \gamma_e\tau P_AP_B(H_A - H_B)^2. \qquad (6)$$

(c) Intermediate exchange. Fig. 3 shows that, with increase of the frequency of the exchange, the lines are displaced towards the centre of the spectrum and become broadened. This shift is unambiguously related to the lifetime of the forms involved in the exchange by the following expression[10]:

$$(\Delta H_0^2 - \Delta H_{exch}^2)^{1/2} = \sqrt{2}/\gamma_e\tau, \qquad (7)$$

where ΔH_0 and ΔH_{exch} are the distances between the lines in the absence and presence of exchange respectively.

The two lines begin to merge into a single line when the exchange frequency is close to the frequency difference $(\omega_A - \omega_B)$. For this reason, the order of magnitude of the exchange frequency may be estimated also from the instant when the two lines merge. The relation

$$1/2\tau = (\omega_A - \omega_B)/4\sqrt{2} \qquad (8)$$

corresponds to this so called intermediate exchange condition. If the frequency units are replaced by magnetic field units in oersteds, it is easy to show that

$$\nu_{exch} = 1/2\tau = 6.25 \cdot 10^{-8}(H_A - H_B). \quad (9)$$

Thus the theory establishes an unambiguous relation between the experimental parameters of the spectrum (the widths and distance between the lines) and the kinetic parameters of the system investigated (ν_{exch} or τ).

The above relations were obtained for the simplest model where two identical EPR lines with the resonance values of the magnetic field H_A and H_B correspond to the two forms of the radical (A and B). However, in practice cases are more frequently encountered where chemical exchange entails exchange between definite HFS components within the complex EPR spectrum. The simplest instance of such exchange was examined qualitatively above in relation to the vinyl radical. The quantitative relation between the exchange frequency and the broadening of the HFS components involved in the exchange in the region of rapid and slow chemical exchange is given by the following expressions[10]:

$$\nu_{exch} = \frac{\gamma_e (\Delta a)^2 (\Delta M_I)^2}{8\Delta (1/T_2)} \text{ (rapid exchange)}, \quad (10)$$

where Δa is the difference between the HFS constants for the forms involved in the exchange and ΔM_I the difference between the projections of the linear spins;

$$\nu_{exch} = \Delta (1/T_2)\, \gamma_e \text{ (slow exchange)}. \quad (11)$$

If the probabilities of the formation of A and B are different and equal to P_A and P_B respectively, then Eqn. (10) is transformed into

$$(\nu_1 + \nu_{-1}) = \frac{\gamma_e P_A P_B (\Delta a)^2 (\Delta M_I)^2}{\Delta (1/T_2)}, \quad (12)$$

where ν_1 and ν_{-1} are the rates of the forward and reverse reactions.

In practice the broadening of the HFS lines due to exchange is estimated from the amplitude of the lines, which is inversely proportional to the square of the width and is thus extremely sensitive to changes in the exchange frequency.

III. DYNAMIC EFFECTS OF THE REDISTRIBUTION OF THE UNPAIRED ELECTRON DENSITY IN RADICAL-ANIONS (CATIONOTROPISM)

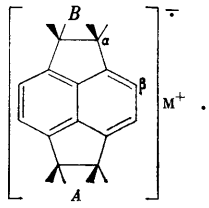
The phenomenon of the dynamic redistribution (depending on the external conditions) of the unpaired electron density between chemically equivalent parts of the molecule is frequently observed in bifunctional radical-anions. The main cause of such redistribution is cationotropism—the transfer of the cation from one functional group to another. In most organic solvents the radical-anions form ion pairs which are weakly dissociated into the free ionic species. In bifunctional radical-anions the cation is located in the vicinity of one of the two functional groups and the symmetrical distribution of unpaired electron density characteristic of the free radical-ion is thus disturbed.

The rate of cationotropic migration determines the form of the EPR spectrum to the extent that it corresponds to the conditions of rapid or slow exchange. The rate of cationotropic migration is determined in its turn by several factors: the chemical nature of the anion and cation, the solvating capacity of the solvent, and temperature.

In the study of a specific radical-anion it is usually possible to alter, within certain limits, the influence of these factors on the rate of the process and to observe how this is manifested in the EPR spectra.

Studies of this kind made it possible to put forward definite hypotheses concerning the mechanism of the dynamic delocalisation of the unpaired electron in bifunctional radical-anions. The term dynamic delocalisation is adopted to emphasise the molecular nature of the motions leading to the redistribution of the unpaired electron density between functional groups. Dynamic delocalisation is in a certain sense equivalent to a chemical reaction the only result of which is the transfer of the cation and electron density between functional groups. Analysis of the specific broadening of EPR lines makes it possible to obtain the kinetic characteristics of chemical reactions of this type.

The dynamic manifestations of cationotropism in the EPR spectra of radical-anions were observed for the first time by de Boer and Mackor[11] in relation to pyracene:



Using various solvents 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (2-MeTHF), metals (Li, Na, and K), and temperatures, de Boer and Mackor found that the form of the spectra, the line widths, and the constants for the hyperfine interaction with the metal cations depend markedly on the conditions used in the observations. In DME, the solvating properties of which are more pronounced than those of THF and 2-MeTHF, spectra characteristic of the "free" pyracene radical-anion with a symmetrical distribution of the unpaired electron density relative to the symmetry axes of the molecule were observed for all the cations employed. Indeed the structure of the ion pair in DME appears to be that of a solvent-separated ion pair. In 2-MeTHF a strong interionic interaction is observed, being manifested by a breakdown of the symmetry of the spin density distribution. The constants for the hyperfine interaction of the unpaired electron with the protons of the CH_2 groups and aromatic β-protons localised in the vicinity of position A differed somewhat from the constants for the protons in the vicinity of position B. When sodium was used as the reducing agent in 2-MeTHF, hyperfine interaction with the sodium nucleus was observed in addition to the proton hyperfine structure, which indicates unambiguously the formation of a contact ion pair. When potassium was used in THF, a pattern involving the alternation of line widths was observed, which was attributed to the migration of the cation between positions A and B in the pyracene molecule. In this case there was splitting due to the interaction with the potassium nucleus, which made it possible to assign the above phenomenon unambiguously to the migration of the cation within the ion pair and to rule out intermolecular interactions.

The data discussed in this section have been classified in accordance with the nature of the functional groups.

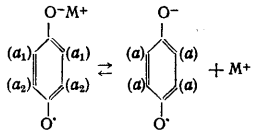
1. Semiquinones

The phenomena of ion association and cationotropism have been widely investigated in relation to semiquinone radical-anions. The use of ethereal solvents and alkali metals as reducing agents made it possible to follow and investigate quantitatively the kinetics of cationotropic migration.

Lucken [12] observed that the lithium salt of *p*-benzosemiquinone in anhydrous t-butyl alcohol gives rise to an EPR spectrum which in no way resembles that obtained previously [13]. Instead of five lines with binomial intensity ratios, Lucken recorded a spectrum comprising nine lines with the intensity ratios 1 : 2 : 2 : 1 : 4 : 1 : 2 : 2 : 1. This implies that the protons in the *p*-benzosemiquinone radical-anion have become non-equivalent in pairs; the relations between the HFS constants are as follows:

$$a_1 \neq a_2 \text{ and } a_1 \neq a,\ (a_1+a_2)/2 = a.$$

The breakdown of symmetry in the distribution of the unpaired electron density is associated with the formation of ion pairs in which the cation is linked to one of the oxygen atoms:



It has been observed [14] that, depending on the conditions, apart from the nine- and five-line spectra, other spectra are also recorded and can be used to follow the smooth transition between the extreme states of the ions; the alternation effects are clearly manifested in these intermediate spectra. Initially there were two views concerning the nature of the phenomena responsible for the alternation of line widths in the spectrum of the *p*-benzosemiquinone radical-anion. Khakhar et al. [15] believed that the alternation is associated with the equilibrium between ion pairs separated by solvent molecules and contact ion pairs and not with the dynamics of the migration of the cation. They attributed the observed alternation pattern to a superposition of the spectra of different ion pairs. Careful analysis of the line form showed subsequently [16] that the observed line width alternation pattern is in fact due to the migrations of the cations between oxygen atoms.

Oakes and Symons [17] investigated the influence of the solvent, the cation, and temperature on the EPR spectra of *p*-benzosemiquinone, durosemiquinone, and different 2,6-disubstituted semiquinones. The solvents employed were t-pentyl alcohol, t-butyl alcohol, DME, and THF, and the counterions were H^+ (hydroxy-radical), Li^+, Na^+, K^+, Rb^+, Cs^+, and $(n\text{-}Bu)_4N^+$. No migration of hydrogen between the oxygen atoms was observed for the hydroxy-radicals derived from *p*-benzosemiquinone and durosemiquinone, and in all the solvents a static pattern was found. In alcohols the lithium cation associated with *p*-benzosemiquinone and durosemiquinone radical-anions migrates at a rate corresponding to slow exchange (the lifetime of the cation near one of the oxygen atoms is $\tau = 5 \times 10^{-7}$ s). The rates of migration of the Li^+ cation in DME and THF correspond to a static pattern ($\tau = 10^{-6}$ s). In alcohols the Na^+ cation migrates at a rate corresponding to the intermediate case ($\tau = 10^{-7}$ s). Depending on the temperature, situations corresponding both to the intermediate case (+25° C) and to the static case (−60° C) are observed in ethers. The frequencies of the migration of the K^+ cation proved to be higher in all the solvents than those for Li^+ and Na^+ and, depending on the conditions, correspond to rapid, intermediate, and slow exchange processes. Oakes and Symons [17] note that the rate of migration of the cation between the oxygen atoms depends strongly on the substituents in the semiquinone:

$$2,3,5,6H \simeq 2,3,5,6\text{-Me} < 2\text{-Me} < 2,6\text{-di-Me} < 2,6\text{-di-t-Bu}.$$

The lifetimes of the cation in the vicinity of one of the oxygen atoms can be arranged in the same sequence and the migration frequencies fall in the opposite sequence. The introduction of substituents makes the oxygen atoms significantly non-equivalent, which leads to the preferential localisation of the cation in the vicinity of one of them and to a decrease of the exchange frequency.

The study of the EPR spectra at different temperatures made it possible to examine the effect of the cation and the solvent on the activation energy for the migration of the metal cation. Fig. 4 illustrates two spectra of K-*p*-benzosemiquinone [18] in DME at two temperatures; the alternation of line widths is seen at −30° C. The contributions of the cation exchange process to line width may be estimated by analysing the line intensities, and the exchange rate constants [19] and activation energies may be calculated (E = 3.4 ± 1 kcal mole^{-1}, $\lg A$ = 9.5 ± 0.5). The activation energy for cation migration varies within wide limits. Table 1 presents kinetic data for the intramolecular migration of the cation in the ion pair formed by the durosemiquinone radical-anion [20,21]. The quantity $\Delta a_H(CH_3)$ (the difference between the two observed HFI constants in the static configuration) increases with temperature, while the mean of the two HFI constants remains unchanged (1.94 ± 0.03 G). For a given series there is a linear relation between the change in the free energy of activation $\Delta G^{\neq}$ and $\Delta a_H(CH_3)$. The negative activation entropy shows that the degree of order in the activated state is greater than that in the reactants and that the activated complex is more solvated than the ion pair.

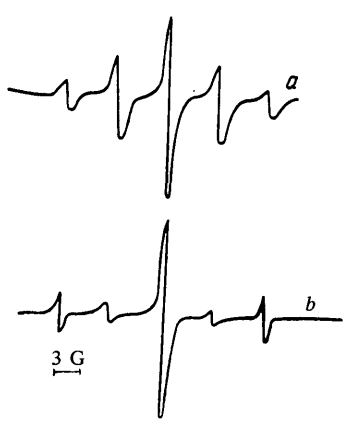
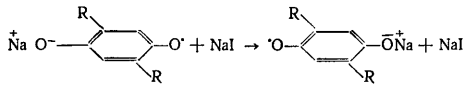


Figure 4. The EPR spectrum of the ion pair comprising the *p*-benzosemiquinone radical-anion and the potassium cation in DME different temperatures (°C): *a*) 20°; *b*) −30° C. [18]

The migration of the cation from one oxygen atom to the other in the semiquinone radical-anion may occur as a bimolecular process. Line width alternation effects in

the EPR spectrum of the Na–2,5-di-t-butyl-*p*-benzosemiquinone radical-ion pair were observed[22] following the addition of NaI to a solution in THF. The authors found from the temperature dependence of the rate constant for the process



(R = t-butyl).

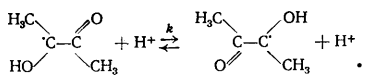
that the activation energy is 2.5 kcal mole^{-1} and the pre-exponential factor is 5.6×10^{10} litre mole^{-1}s^{-1}.

Table 1. The activation energies and pre-exponential factors for the cation migration in durosemiquinone radical-anions (D).

Ion pair	Solvent	E, kcal mole^{-1}	$10^{-10}A$, s^{-1}
Na-D	DME	3.57±0.20	0.12
Na-D	THF	5.61±0.23	0.47
K-D*	DME	5.27	14
K-D*	THF	7.39±0.52	470
Cs-D	DME	4.46±0.27	54
Cs-D	THF	4.82±0.28	660
Cs-D	MeTHF	3.70±0.25	6.9
K-D	DME	5.05±0.34	52
K-D	THF	6.2±0.20	270

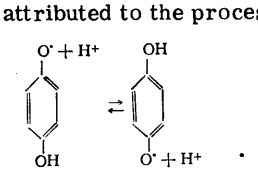
*Data from Prahananda et al.[21]

A similar mechanism has been proposed to explain the acid-catalysed proton transfer in the monoprotonated *trans*-semidione radical[23]. The authors obtained it in a water flow system at 23°C by one-electron reduction of diacetyl. At pH 0.5 they observed a spectrum consisting of a binomial septet (a_H = 8.3 G); at pH 1 appreciable line width alternation was observed in the spectrum. At pH 2 the pronounced alternation converts the septet into a 1 : 9 : 9 : 1 quartet with an HFI constant of 16.6 G. At pH 3 the two methyl groups become non-equivalent and a splitting due to the one proton of the OH group appears: $a_H(CH_3)$ = 12.8 G; $a_H(CH_3)$ = 3.8 G; $a_H(OH)$ = 2.0 G. This result was attributed to acid-catalysed proton transfer between oxygen atoms:

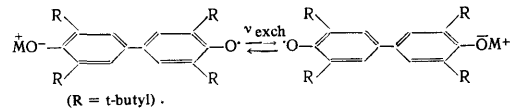


The rate constant is 4.53×10^9 litre mole^{-1}s^{-1}.

Smith and Carrington[24] observed a dependence of the line width on pH in the spectrum of the monoprotonated *p*-benzosemiquinone radical-anion (the 4-hydroxyphenoxy-radical), which they attributed to the process



There exists yet another factor which may influence the exchange frequency. It is the distance between the oxygen atoms, which may be altered by employing quinones of different structures. We investigated[25] the EPR spectra of the radical-anions derived from 3,3′,5,5′-tetra-t-butyldiphenylquinone (TBDP). The observed line width alternation patterns made it possible to measure the cation exchange frequencies:

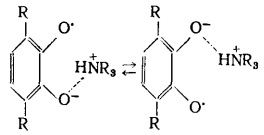


(R = t-butyl).

The order of magnitude of the values of ν_{exch} for the TBDP radical-anion corresponds to that of the cation migration frequencies in *p*-benzosemiquinones, although the cation localisation centres in the radical-anion which we investigated are separated by a much greater distance. The cause of this phenomenon is apparently the fact that the cation migration frequency is determined mainly by the depth of the energy minima on the potential curves corresponding to the limiting structures and by the distance between these minima. The minima for *p*-benzosemiquinone are fairly close. The energy minima for the "limiting" structures of TBDP are much further apart, although their depth is smaller owing to the extensive conjugation system and this leads to the same cation migration frequencies as in benzosemiquinones.

The *o*-benzosemiquinone radical-anions are systems in which the oxygen atoms are much closer to one another. The EPR spectra of 3,6-di-t-butyl-*o*-benzosemiquinone radical-anions[26] in different solvents, at different temperatures, and in the presence of different metal cations always exhibit a symmetrical unpaired electron density distribution. This implies that the cations either occupy a symmetrical position in relation to the oxygen atoms or migrate at a high frequency.

The use of alkylammonium cations in an ion pair incorporating the 3,6-di-t-butyl-*o*-semiquinone anion leads to effects associated with a dynamic redistribution of the unpaired electron density, which was attributed to the migration of the hydrogen bond between oxygen atoms[27]:

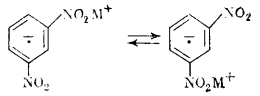


(R = t-butyl).

2. Cationotropism in Ion-Pairs Formed by Dinitrobenzene Radical-Anions and in Certain Other Bifunctional Radical-Anions

Line width alternation effects have been found in ion pairs formed by *o*-, *m*-, and *p*-dinitrobenzene radical-anions[28–33]. The alternation is caused by the migration of the cations between the nitro-groups. Symons and coworkers[18,19] [wrong references?] obtained the *p*-dinitrobenzene radical-anions by the photolysis of a methanol solution containing sodium methoxide. The addition of solvents promoting the formation of ion pairs caused line width alternation. In the *o*-dinitrobenzene radical-anion the sodium cation migrates at room temperature at a frequency corresponding to the rapid exchange conditions. A decrease of temperature to −60°C causes the appearance of the alternation effect. The slow exchange situation is not observed. A similar behaviour has been observed for potassium cations[33]. For caesium cations, only rapid exchange is observed at all temperatures.

Slow exchange is observed in the sodium salt of the *m*-dinitrobenzene radical-anion at all temperatures. In the potassium salt at low temperatures there is slow exchange but at 0°C alternation effects appear. In the EPR spectra of the caesium and rubidium salts a transition is observed from slow exchange at low temperatures to a distinct line width alternation pattern at room temperature:

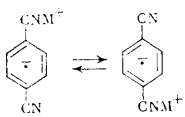


The formation of ion pairs comprising the pyrazine radical-anion and the sodium cation has been investigated[34]:



At room temperature the EPR spectrum reveals hyperfine interactions with the two nitrogen nuclei (a_N = 7.14 G), with the four protons (a_H = 2.70 G), and with the sodium nucleus (a_{Na} = 0.55 G). At lower temperatures alternation effects associated with the migration of the cation appear. The process activation energy is E_a = 7.1 ± 0.5 kcal mole^{-1} and $A = 2 \times 10^{13}$ s^{-1}. The activation energy for the caesium cation proved to be much higher: E_a = 15 kcal mole^{-1}.

Nakamura[35] investigated the exchange of the sodium cation in the terephthalonitrile radical-anion:



The activation energy in THF proved to be E_a = 5 ± 1 kcal mole^{-1} for sodium and E_a = 3.7 ± 0.5 kcal mole^{-1} for potassium.

3. The Radical-Anions of Bridged Compounds

Numerous studies have been devoted to the distribution of the unpaired electron density in systems having the general structure $[Ar-X-Ar]^{\cdot-}M^+$, where Ar are either aromatic radicals or π-electron functional groups and X are isolating bridges of different lengths and structures[36]. The interest in these systems is due to the hypothesis that the study of the distribution of their unpaired electron density can yield information about the ability of the X groups to "transmit" the unpaired electron from one aromatic fragment to the other. However, later studies showed that this simplified electron transfer mechanism, which depends only on the transmittivity of the –X– bridge, does not take into account the formation of ion pairs. Studies of the EPR spectra of the radical-anions $[Ar-X-Ar]^{\cdot-}M^+$ showed that the nature of the solvent and temperature have a strong influence on the distribution of the unpaired electron density and on the frequency of electron transfer between the aromatic fragments.

The hypothesis that the migration of the metal cation plays a decisive role in the dynamic delocalisation of the electron in the radical-anions of bridged compounds was not immediately demonstrated experimentally. The clearest example is provided by the study of Gerson and Martin[71], who investigated the EPR spectra of diphenylmethane and *p*-deuterodiphenylmethane in DME and showed that the unpaired electron is delocalised over the two benzene rings. It is believed[72,73] that the annular 1,3-interaction between the benzene rings determines the mechanism of the electron transfer between them. However, this idea conflicts with data which the same authors obtained in a study of the EPR spectrum of the diphenylmethane radical-anion in MeTHF.[72] A static picture, corresponding to the localisation of the unpaired electron in one benzene ring, was observed, which is inconsistent with the concept of the decisive role of annular 1,3-interactions.

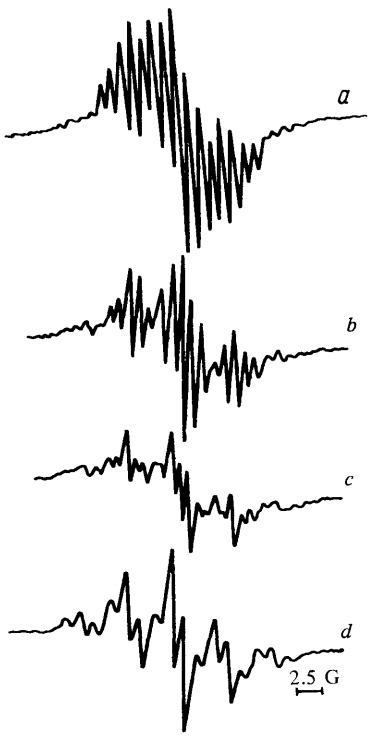
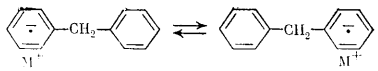


Figure 5. The EPR spectrum of the ion pair comprising the diphenylmethane radical-anion and the potassium cation in a mixture of diethyl ether and 10% of hexamethylphosphoramide at different temperatures (°C): *a*) –70; *b*) –100; *c*) –110; *d*) –127.

The authors of the present review investigated the exchange of the unpaired electron in the diphenylmethane radical-anion in various solvents and at various temperatures[37-40]. The rapid exchange condition holds in DME (K^+ cation) over the entire temperature range. In a 1 : 1 DME : THF mixture at –70°C there is also a rapid exchange. When the temperature is reduced to –100°C, alternating line width effects appear. As a result, the relatively complex EPR spectrum is converted into a spectrum in which five principal lines are distinctly visible; EPR spectra of this type usually arise from the radical-anions of alkylbenzenes[36]. Analysis of the hyperfine structure of the spectrum showed that the exchange frequency corresponds to the intermediate case in relation to the hyperfine interaction with the *ortho*- and *meta*-protons; the rapid exchange condition holds in relation to *para*-protons. The exchange frequency is $\nu_{exch} = 10^{12} \exp(-4000/RT)(s^{-1})$. The slow exchange condition was achieved[40] when ethyl ether containing 10% of hexamethylphosphoramide was used

as the solvent. Fig. 5 presents the EPR spectra corresponding to the conditions of the rapid (*a*), intermediate (*b*) and (*c*) and slow (*d*) exchange processes, the exchange frequency being given by $\nu_{exch} = 2.3 \times 10^{13} \exp(-4300/RT)$.

The nature of the influence of the solvent and temperature shows convincingly that the solvating capacity of the solvent determines the mobility of the metal cation on which the fulfilment of rapid or slow exchange conditions depends. A distinctive feature of the diphenylmethane radical-anion compared with the systems discussed above is the separation of the functional groups (benzene rings) by a considerable energy barrier due to the methylene group. As a result of this feature, the unpaired electron is fully transferred from one benzene ring to the other:



In *p*-benzosemiquinone radical-anions the migration of the cation causes only a partial redistribution of electron density between oxygen and carbon atoms within the limits of the common π-electron system.

Similar effects of temperature and the solvent were observed for other radical-anions—those of $\alpha\alpha'$-dinaphthylmethane and 1,2-di(α-naphthyl)ethane[37]. A similar situation has been observed in a study of exchange via the $>Si(C_2H_5)_2$ group in the radical-anion $Ph_2Si(C_2H_5)_2^{-}K^{+}$ in THF:[41] $\nu_{exch} = 10^9 \exp(-2800/RT)\ (s^{-1})$.

Apart from the "two-well" systems discussed above, more complex systems have been investigated—"three-well" (triphenylmethane radical-anions)[42] and "four-well" systems (tetraphenylsilane radical-anions)[41]. Fig. 6 presents the EPR spectrum of the tetraphenylsilane radical-anion in THF (K^+ cation). The spectrum at −40°C (*a*) consists of the principal quintet arising due to four *para*-protons ($a_p = 2.2$ G). Each line of the quintet is split into nine lines due to the eight *ortho*-protons ($a_o = 0.8$ G). At −140°C the spectrum is converted into a poorly resolved doublet with a splitting of 8 G, which indicates the localisation of the unpaired electron in one benzene ring only.

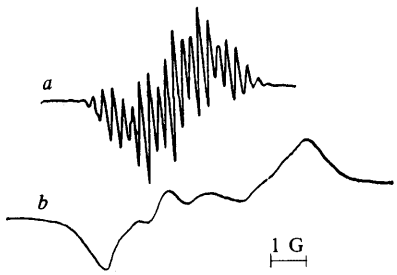


Figure 6. The EPR spectrum of the tetraphenylsilane radical-anion in THF at different temperatures (°C): *a*) −40; *b*) −140.

The systems considered hitherto have equivalent cation localisation centres. In the *p*-dibenzylbenzene radical-anion the two extreme benzene rings are structurally different from the central ring and the probability of finding the metal cation near the centre of the molecule should be different from the probability of finding the cation at its edges[43]. This should be the case primarily in the region of slow exchange, where the spectrum corresponds to the localisation of the cation near one of the benzene rings:

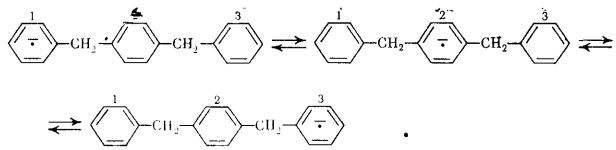


Fig. 7 illustrates one of the spectra recorded in THF, DME, and their mixtures (potassium cation) at −60° and −70°C. A decrease of temperature and the addition of ethyl ether cause a transformation of this fairly complex spectrum into a quintet characteristic of *p*-dialkylbenzenes. Analysis of the spectrum shows that at a low temperature the cation is localised near the central benzene ring. The principal quintet splitting of 4.67 G is due to the interaction with the four protons of the central benzene ring and the additional splitting (1.14 G) is due to the interaction with the four protons of the two methylene groups. Analysis of the line width alternation effects showed that the potassium cation migration frequency at −60° and −70°C between benzene rings *1*, *2*, and *3* and the corresponding unpaired electron delocalisation frequency are within the following limits (s^{-1}): $10^7 > \nu^{1-3} > 3 \times 10^6\ s^{-1}$; $\nu^{1-2} = \nu^{2-3} > 10^7\ s^{-1}$. At −100°C the exchange frequency is $\nu^{1-2} = \nu^{2-3} > 10^7\ s^{-1}$.

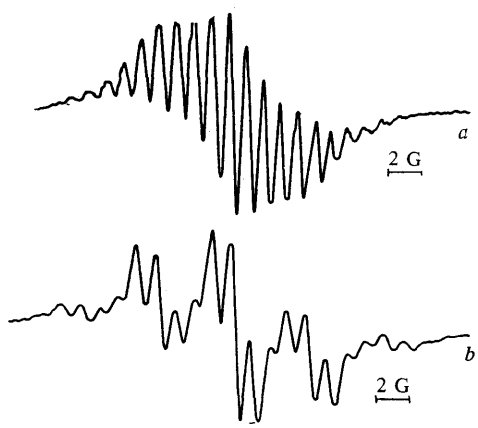


Figure 7. The EPR spectrum of the ion pair comprising the *p*-dibenzylbenzene radical-anion and the potassium cation in THF, DME, and their mixture at −60° and −70°C (*a*) and in a mixture of 90% of diethyl ether and 5% of hexamethylphosphoramide at −100°C (*b*).

Non-aromatic bridged systems have also been investigated. Syrkin et al.[44] found that in the electrochemical generation of difluorodinitromethane anions there is rapid electron exchange between the nitro-groups. On the other hand, a static picture involving the localisation of the unpaired electron in one of the nitrated aromatic components of the molecule is observed in the di-$\alpha\alpha$-difluoro-di-(4-nitrophenyl)methane[45]. A static picture is also characteristic of the dibenzyl[46] and di-(4-nitrophenyl)methane radical-anions[47].

4. The Mechanism of the Dynamic Delocalisation of Electrons in Bifunctional Radical-Anions

Before considering the mechanism of the dynamic delocalisation of the electron (cationotropism), it is necessary to examine the causes responsible for the asymmetric disposition of the cation in the ion pairs formed by bifunctional radical-anions. If the exchange interaction is fully disregarded, then the nature of the bond between the anion and the cation in the ion pair reduces exclusively to electrostatic forces. A simple calculation shows that the Coulombic interaction energy between the cation and anion increases if the cation is located near one of the functional groups, to which an excess (compared with the free ion) negative change density is drawn under the influence of the electric field of the cation. Thus an asymmetric structure of the ion pair formed by a radical-anion having two functional groups is energetically more favourable than the symmetrical disposition of the cation. An asymmetric distribution of the unpaired electron density leads to some loss of exchange energy but in the case of bridged compounds the latter is apparently small; in other cases the loss may be appreciable. It appears that for this reason it is impossible to ensure the location of the unpaired electron in a single benzene ring of the biphenyl radical-anion by selecting appropriate conditions. It is quite likely that in this case the loss of exchange energy owing to the separation of the π-electron systems of the benzene rings is not compensated by the gain in Coulombic energy. The degree of redistribution of the unpaired electron density in a particular radical-anion as a function of the nature of the cation and the solvent is a qualitative measure of the bond strength in the ion pair.

Several models have now been proposed for the description of the dynamic delocalisation of the unpaired electron. McConnell[48] considered the delocalisation of the unpaired electron in the radical-anions of $\alpha\omega$-diphenylalkanes. The interaction with the medium was taken into account with the aid of the formal effect involving the self-localisation of the charge without taking into account the structure of the ion pairs. McConnell analysed the ability of $(-CH_2-)_n$ bridges of different lengths to transmit an electron.

Claxton[49] considered the exchange of the cation between the nitrogen atoms of the pyrazine radical-anion and postulated the liberation of the cation from the solvent cage containing the radical-anion. After the cation leaves the cage, the radical-anion rotates in the latter independently of the cation. This rotation ensures the migration of the cation when it re-enters the solvent cage. By studying the reaction coordinate, Claxton found that the cation moves from one atom to another, deviating from the plane of symmetry of the molecule.

It is noteworthy that both models considered do not take into account the specific structure of ion pairs. Presumably the mechanisms of the dynamic delocalisation of the unpaired electron in bifunctional aromatic radical-anions and in bridged compounds have common features. These features are associated with the decisive role of the mobility of the cation. The difference between them is that in bifunctional aromatic radical-anions there are no energy barriers preventing the delocalisation of the electron, since the positions of the cations are linked by the common π-electron system. At the present time the mechanism of the dynamic delocalisation cannot be treated in isolation from modern ideas concerning the structure of ion pairs. We believe that the dynamics of the migration of the cation is indissolubly linked to the interconversions between contact ion pairs and ion pairs separated by solvent molecule.

Evidently the Coulombic interaction between the radical-anion and the cation in a solvent-separated ion pair is much weaker than the interaction in a contact ion pair. The cation in a solvent-separated ion pair is less able to distort the distribution of the unpaired electron over the radical anion. Thus for the interconversions of ion pairs having different structures to play a significant role in the dynamic delocalisation mechanism, they must take place with frequencies of approximately 10^7–10^8 s^{-1}. Such frequencies are indeed observed in the reactions of ion pairs[50]. There is a complete parallelism between the influences of the nature of the cation and the solvent on the rate of dynamic electron delocalisation and on the interconversions of ion pairs. In solvents such as THF and diethyl ether (DEE), where the formation of contact ion pairs takes place more readily than in DME, dynamic delocalisation processes are much slower than in DME. Analysis of experimental data showed that the activation energy for the migration of the cation is determined by the nature of the ion pair.

Presumably the conversion of a contact ion pair into a solvent-separated one is the initial stage in the cation migration processes. Furthermore, it is necessary that during the lifetime of the solvent-separated ion pair there is sufficient time for the cation to pass to a new location in the radical-anion. The influence of the solvent and the cation on processes associated with the dynamic delocalisation of the unpaired electron in a specific radical-anion reduces mainly to a change of bond strength in the ion pair. On the other hand, in considering different radical-anions, one must take into account the geometrical factors in the locations of the cation. A large distance between them or an unfavourable conformational disposition may increase the time taken for the transfer of the cation to such an extent (static case) that the application of the EPR method to the estimation of the kinetic parameters of the cationotropic migration becomes ineffective.

In the majority of the bifunctional aromatic radical-anions considered above, the functional groups are fairly close and the rate-limiting stage is apparently merely the dissociation of the bond in the ion pair. In the radical-anions derived from bridge compounds, increase of the distance between the locations of the cation leads to a decrease of the delocalisation frequency owing to the longer migration of the cation[39,51].

An unambiguous answer to the question of the ability of bridge groups to transmit an electron cannot be obtained from EPR data, because the delocalisation frequency depends on the mobility of the cation. One can only assume that, in the presence of a small number of units in the bridge group, an exchange interaction (with an intensity corresponding to approximately 10^{-5}–10^{-7} eV), which is necessary to ensure the "intrinsic" exchange frequencies in the "free" radical-anion (approximately 10^9–10^7 s^{-1}), takes place.

The phenomenological picture considered above reflects only the most general features of the exchange processes. In a quantitative treatment of the experimental data for the rates of exchange or the constants for equilibria involving ion pairs of radical anions one frequently encounters additional effects associated with the dependence of the properties of the solvent on temperature[25,52]. Over a wide temperature range, the dielectric constants of solvents vary within broad limits, which leads to appreciable additional shifts in the equilibria between ion pairs having different structures. Change in the properties of the

solvent frequently leads to appreciable deviations from the Arrhenius relation for the rate and equilibrium constants. For this reason, all the activation energies and rate constants for exchange processes as a rule refer to narrow temperature ranges.

IV. DYNAMIC DELOCALISATION OF THE UNPAIRED ELECTRON IN FREE RADICALS

The examples considered in the previous section, which illustrate the cationotropisms in ion pairs formed by radical-anions, constitute the type of tautomerism of radicals which has been investigated in greatest detail and which differs from the classical tautomerism by the migration of ionic and not covalent bonds. The tautomerism of radicals, accompanied by the migration of organic or organoelemental fragments between equivalent positions in radicals and the synchronous redistribution of the unpaired electron density in such species, is considered below.

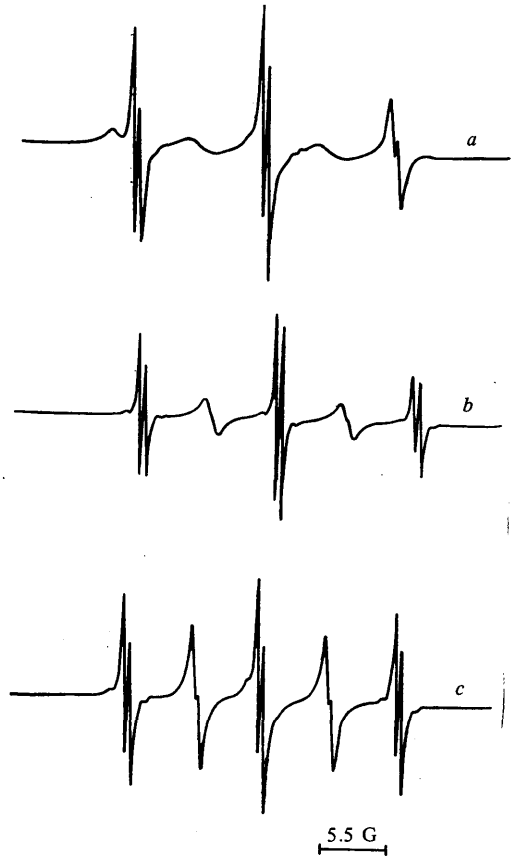
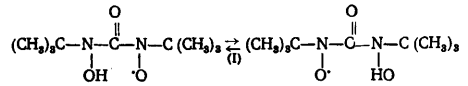


Figure 8. The EPR spectra of radical (I) at different temperatures (°C): *a*) −80; *b*) 0; *c*) 60.

1. Migration of Hydrogen and Deuterium

The simplest examples of this type of tautomerism are the intramolecular migration of hydrogen and deuterium atoms. Analysis of the line width in the EPR spectra[53] demonstrated the possibility of the migration of the hydrogen atom in radical (I) having the following structure:



At low temperatures (−90° C) the EPR spectrum of this radical is a triplet due to the interaction of the unpaired electron with the nitrogen nucleus (a_N = 10.4 G), each component of which is split into a doublet by the proton of the hydroxy-group [a_H(OH) = 0.5 G] (Fig. 8). With increase of temperature, the spectrum is transformed into a quintet (owing to the two equivalent nitrogen atoms) with an HFI constant smaller by a factor of two than the constant due to one nitrogen atom. The energy barrier to the migration of hydrogen is 2.7 ± 0.3 kcal mole^{-1}. The authors of the present review demonstrated almost simultaneously[54,55] the occurrence of the intramolecular migration of hydrogen and deuterium atoms in the 3,6-di-t-butyl-2-hydroxyphenoxy-radical (II):

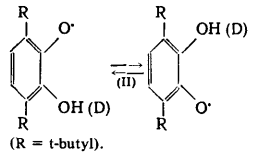


Fig. 9*a* illustrates the EPR spectrum of this radical at 60° C.

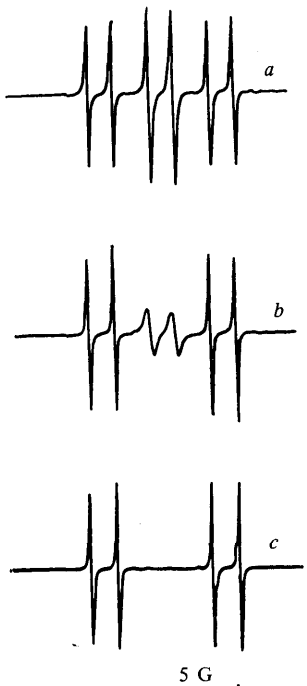


Figure 9. The EPR spectra of radical (II) in toluene at different temperatures (°C): *a*) 60; *b*) 0; *c*) −60.

The triplet (a_H = 3.92 G) is due to the interaction of the unpaired electron with the "equivalent" ring protons; each component of the triplet is split into a doublet by the proton

of the hydroxy-group [a_H(OH) = 1.6 G]. In the spectrum of the analogue of radical (II) deuterated at the hydroxy-group each component of the triplet consists of three lines owing to the interaction of the unpaired electron with the deuterium nucleus [a_D(OD) = 0.26 G] (Fig. 10*a*). With increase of temperature, the central component of the triplet is broadened (the breakdown of the "equivalence" of the ring protons), indicating the inhibition of the intramolecular migration of hydrogen (deuterium) atoms between the oxygen atoms in radical (II).

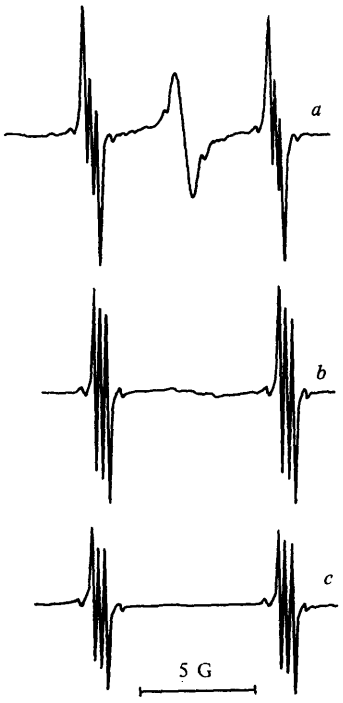


Figure 10. The spectra of radical (II), deuterated in the hydroxy-group, in toluene at different temperatures (°C): *a*) 60; *b*) 0; *c*) −60.

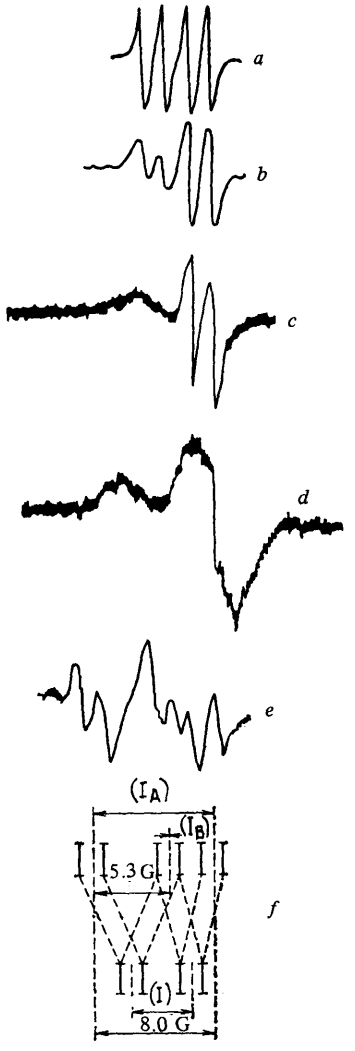
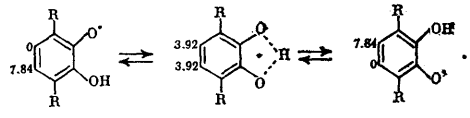


Figure 11. The EPR spectra of radical (V) in diethyl ether at different temperatures (°C): *a*) 100; *b*) 20; *c*) 0; *d*) −20; *e*) −100; *f*) schematic representation of the spectra of radical (V) under slow exchange conditions.

At fairly low temperatures (below −60°C) migration ceases on the EPR time scale (~ 10^{-7} s) and a spectrum corresponding to one of the "frozen" structures (II_A) or (II_B) is observed (Figs. 10*c* and 11*c*). The HFI constants for structures (II_A) and (II_B) (slow exchange) as well as (II_{av}) (rapid exchange) are given below for greater clarity:



(R = t-butyl).

Analysis of the line widths made it possible to determine the kinetic parameters of the migration of hydrogen and deuterium atoms and to estimate the kinetic isotope effect. The frequencies of the intramolecular migration of hydrogen (ν_H) and deuterium (ν_D) atoms in radical (II) are listed below (solvent—heptane):

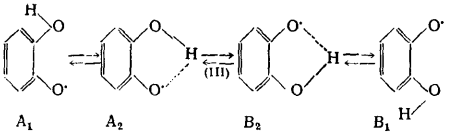
t, °C	$10^{-9}\nu_H$, s^{-1}	$10^{-9}\nu_D$, s^{-1}	ν_D/ν_H (expt.)	ν_D/ν_H (calc.)
20	3.2	0.3	0.08	0.09
60	5.5	0.75	0.14	0.12
80	6.3	1.0	0.16	0.14
120	10.0	2.2	0.22	0.17

Activation energies of 2.9 and 4.5 kcal $mole^{-1}$ respectively were determined from the temperature dependence of ν_H and ν_D. The experimental isotope effect agrees well with the value calculated theoretically from the following expression:

$$\frac{\nu_D}{\nu_H} = \exp\left\{\frac{hc}{2kT}(\tilde{\nu}_{OD} - \tilde{\nu}_{OH})\right\}, \quad (13)$$

where $\tilde{\nu}_{OD}$ and $\tilde{\nu}_{OH}$ are the stretching vibration frequencies of the OD and OH bonds determined from the infrared spectra of sterically hindered phenols. It has been shown[56] that solvents capable of forming hydrogen bonds inhibit the migration of hydrogen in radical (II). The complete set of results obtained made it possible to conclude that the migration of hydrogen atoms has a homolytic mechanism and is in essence an intramolecular radical substitution reaction.

Later Loth et al.[57] observed an analogous effect in the unsubstituted 2-hydroxy-phenoxy-radical (III), the EPR spectra of which exhibit a specific broadening of the lines—a hyperfine structure. However, analysis of the spectra is complicated in this instance by the hindered rotation of the OH bond and the occurrence of the conformers A_1, A_2, or B_1, B_2, which differ in their structures and thermodynamic stabilities:



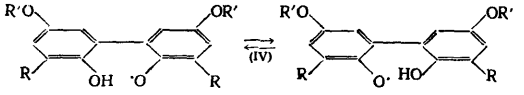
The hydrogen migration frequencies (ν_H) and deuterium (ν_D) in radical (III)[57] are listed below:

t, °C	$10^{-5}\nu_H$, s^{-1}	t, °C	$10^{-5}\nu_D$, s^{-1}
22	191	72	21.4
5	96.1	58	14.8
−25	16.0	38	5.12
−55	1.62	18	1.78

The activation energies are 8.2 ± 0.1 and 9.5 ± 0.5 kcal $mole^{-1}$ respectively. Owing to the possibility of the existence of the above conformers, the migration frequencies of hydrogen and deuterium in radical (III) are much lower than those in radical (II), where the presence of the bulky t-butyl groups prevents the rotation of the OH group, and the radical exists in a form where the hydrogen atom is virtually in the plane of the aromatic ring (of type A_2 or B_2). The sharply reduced migration frequencies in radical (III) may be due to the fact that the rate-limiting stage in the intramolecular transfer is not the dissociation of the OH or OD bonds, but the stage defined by the lifetime of the conformers A_2 or B_2, simulating the transition state in the transfer of hydrogen and deuterium. Analysis of the planar conformers (A_2, B_2) showed that the difference between the O–H and O...H bond lengths is small and amounts to only 0.3 Å.

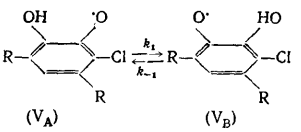
The authors explain the anomalous kinetic isotope effect (approximately 100) for radical (III) by the fact that, apart from the stretching vibrations of the OH and OD bonds, account must be taken of the contributions of all the vibrations characteristic of the CCOH fragment.

The EPR spectra of radicals (IV),



were observed quite recently[58]. The HFI constants of the ring protons and α-hydrogen atoms of the alkoxy-substituents are equivalent in pairs and in the temperature range from −50° to 25°C there is no alternation of line widths. This led the authors to the conclusion that rapid intramolecular processes take place in radicals of this type. It is noteworthy that the HFI constants for the ring protons ($a_H^{3,3}$ = 1.4 G) and the protons in the alkoxy-substituents [$a_H(OCH_3)$ = 0.83 G] are small and that in this case the rapid exchange condition may be fulfilled for the usual exchange frequencies (~ 10^7–10^8 s^{-1}).

The examples discussed above illustrate the simplest instances of degenerate tautomerism—the migration of hydrogen and deuterium atoms between equivalent positions in the radical. The intramolecular migration of hydrogen and deuterium atoms in the 3,5-di-t-butyl-2-chloro-6-hydroxyphenoxy-radical (V), which constitutes the simplest example of non-degenerate tautomerism:



has been investigated[59]. In diethyl ether at low temperatures the EPR spectrum of radical (V) is a doublet (a_H = 3.3 G) due to the interaction of the unpaired electron with a ring proton; each component of the doublet contains two lines (a_H = 1.5 G) owing to the hydroxyl proton (Fig. 11*a*). With decrease of temperature, the downfield component of the ring proton doublet is broadened, virtually disappearing at 0°C (Figs. 11*b* and 11*c*). On further decrease of temperature, the hydroxyl doublet coalesces (Fig. 11*d*) and at −100°C the observed spectrum consists of a superposition of two signals with slightly different g factors (Fig. 11*e*): a doublet with a_H = 8.0 G, each component of which is split in two (a_H = 1.5 G), and a second doublet a_H = 1.5 G.

The above changes in the spectra are fully reversible when the temperature is altered and indicate the occurrence of dynamic effects due to the intramolecular migration of a hydrogen atom between oxygen atoms. At higher and lower temperatures respectively the conditions for rapid and slow exchange between forms (V_A) and (V_B) obtain. Fig. 11*f* illustrates schematically these two instances for equality of the mole fractions of forms (V_A) and (V_B). This interpretation of the EPR spectra is confirmed by the comparative analysis of the spectrum of the deuterated analogue of radical (V). The doublet with a_H = 8.0 G refers to the (V_B) form, while the spectrum without HFI due to the ring proton refers to the (V_A) form. Analysis of the temperature dependence of the HFI of the ring proton in the high-temperature spectra (rapid exchange) made it possible to estimate the constant for the equilibrium between forms (V_A) and (V_B), from the expression

$$K_p = \frac{\alpha}{1-\alpha} = \frac{\tilde{a}}{a_{V_A} - \tilde{a}}, \qquad (14)$$

where $\tilde{a} = \alpha a_{V_A} + (1-\alpha)a_{V_B}$, α is the mole fraction of form (V_A), and a_{V_A} = 8.0 G and a_{V_B} = 0 G are respectively the HFI constants for the ring proton in the corresponding forms. The thermodynamic parameters obtained in this way are $K_p(20°)$ = 0.83 and ΔH = −0.33 kcal $mole^{-1}$ (toluene). The greater thermodynamic stability of form (V_A) follows from the fact that the electrons in the outer shell of the chlorine atom, located in this form in the *ortho*-position relative to the univalent oxygen atom, interact more effectively with the unpaired electron of radical (V), increasing its stabilisation energy.

The thermodynamic data obtained and analysis of the broadening in the EPR spectra made it possible to obtain the rate constants (k_1 and k_{-1}) for the reversible proton transfer between forms (V_A) and (V_B). The hydrogen and

deuterium migration frequencies for radical (V) in toluene are listed below:

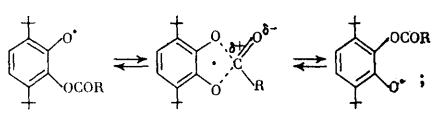
t, °C	$10^{-8}k_1$(H), s^{-1}	$10^{-7}k_1$(D), s^{-1}	k_1(D)/k_1(H) (expt.)	k_1(D)/k_1(H) (calc.)
20	4.1	3.0	0.07	0.09
40	6.5	5.6	0.09	0.11
60	9.5	9.6	0.10	0.12
80	19	25.0	0.13	0.14

The activation energies are respectively 4.1 ± 0.5 and 5.7 ± 0.5 kcal $mole^{-1}$. As for radical (II), the kinetic isotope effect is described satisfactorily by Eqn. (13). In solvents capable of forming hydrogen bonds (for example in diethyl ether) the constants K_p hardly change, but the rate constants k_1 and k_{-1} decrease appreciably, which makes it possible to observe the spectra of the individual species at low temperatures corresponding to the slow exchange conditions.

2. Migration of Fragments with Group IV Elements

In the search for further examples of the tautomerism of radicals, the authors of the present review turned to radicals containing substituents with Group IV elements (carbon and tin). The migration of the methyl group between oxygen atoms in the 3,6-di-t-butyl-2-methoxyphenoxy-radical (VI)† was not observed up to 200°C. The hyperfine structure of the EPR spectrum of this radical does not exhibit a specific broadening of the lines over the entire temperature range; the spectrum consists of a doublet of doublets due to the interaction of the unpaired electron with the *para*-proton (a_H = 8.65 G) and the *ortho*-protons (a_H = 1.0 G) of the aromatic ring; each component being a quartet owing to the protons of the methyl group [$a_H(CH_3)$ = 1.37 G].

The intramolecular migration of carbon-containing groups with EPR frequencies has been observed for acylotropic migration in 2-acyloxy-3,6-di-t-butylphenoxy-radicals[60,61]:



R = $COCH_3$ (VII), COC_2H_5 (VIII), $COCH_2Br$ (IX), $COCH_2C_6H_5$ (X), or $COCH(C_6H_5)_2$ (XI).

The EPR spectrum of radical (VII) is illustrated in Fig. 12. The doublet with a_H = 10.2 G is due to the interaction of the unpaired electron with the ring proton in the *para*-position relative to the "univalent" oxygen atom. Each component of this doublet is split into two lines due to the *meta*-proton of the aromatic ring (a_H = 1.95 G). The above interpretation of the spectrum is fully consistent with the unpaired electron density distribution characteristic of phenoxy-radicals: an appreciable positive spin density is observed in the *para*-position of the phenoxy-ring and the HFI constant is between −8 and 10 G, while in the *meta*-position the spin density is negative and the HFI constant is between 0.5 and 2.2 G. The EPR spectra of radicals (VIII)–(XI) are analogous to the spectrum of radical (VII).

With increase of temperature (to 120°C) a distinct broadening of the extreme HFS component is observed in the EPR spectra of radicals (VII)–(X) (Fig. 13) due to the migration of the acyl group between the oxygen atoms. It is noteworthy that the broadened lines are not displaced, i.e. the slow exchange condition is fulfilled. Under the rapid exchange condition, which does not obtain in the given experiment, the EPR spectra of radicals (VII)–(X) should consist of a triplet, due to the "equivalent" ring protons, with an HFI constant of (10.2–1.95)/2 = 4.1 G. In the case under consideration, corresponding to slow exchange, the spectral lines with overall nuclear spin projections $M_I(+1/2, +1/2)$ and $M_I(-1/2, -1/2)$ hardly change their positions, while the lines with $M_I(+1/2, -1/2)$ and $M_I(-1/2, +1/2)$, should be converted into the line with $M_I(0)$ in the spectrum corresponding to rapid exchange. The opposite signs of the nuclear spin projections of the aromatic ring protons are due to the opposite signs of the spin intensities at the corresponding carbon atoms, which leads to the broadening of the extreme HFS components[60].

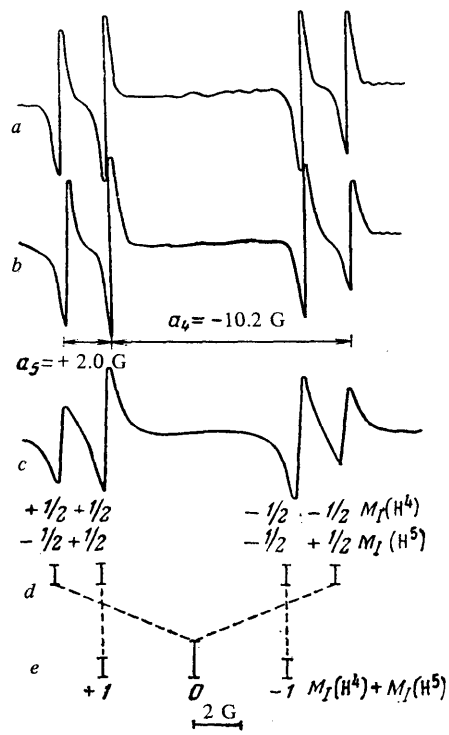


Figure 12. The EPR spectra of radical (VII) in benzene at different temperatures (°C): *a*) 80; *b*) 100; *c*) 120; *d*) and *e*) schematic representation of the spectra under the conditions of slow and fast exchange respectively.

The kinetic parameters of the acylotropic migration in radicals (VII)–(XI) were calculated on the basis of the analysis of the line width[61]. The influence of the substituent on the kinetic parameters of the acylotropic migration

†A.I. Prokof'ev, T.I. Prokof'eva, N.N. Bubnov, S.P. Solodovnikov, I.S. Belostotskaya, V.V. Ershov, and M.I. Kabachnik, Dokl. Akad. Nauk SSSR (in the Press).

in radicals (VII)–(XI) (solvent—toluene) is illustrated below:

Radical	Acyl	$10^{-4}\nu(20°)$, s^{-1}	$10^{-12}\nu_0$, s^{-1}	$E_{act} \pm 1.0$, kcal $mole^{-1}$
(VII)	$COCH_3$	1	9.0	11.4
(VIII)	COC_2H_5	1	11.0	13.0
(IX)	$COCH_2Br$	26	21.0	10.7
(X)	$COCH_2C_6H_5$	10	0.6	9.45
(XI)	$COCH(C_6H_5)_2$	3	2.3	10.7

Evidently, as the electron-accepting properties of the substituents in the acyl group become more pronounced, the exchange frequencies increase and the energy barriers diminish. The data for radicals (X) and (XI) show that the mass of the migrating fragment plays a definite role. The results suggest that the facilitation of the migration of the acyl group following the enhancement of the electron-accepting properties of the substituents is due to the electron deficiency arising at the carbonyl carbon atom, which favours the formation of a polar transition state. The migration of acyl groups apparently proceeds via this state. The above mechanism of acylotropic migration is supported by positive acid catalysis. It has been shown for radical (VII)[61] that in the presence of one mole of trifluoroacetic acid the energy barrier decreases by a factor of two, and the frequency of migration of the acyl group increases by a factor greater than 100. The electron deficiency at the carbonyl carbon atom occurs as a result of the protonation of the carbonyl group in the acid–radical complex.

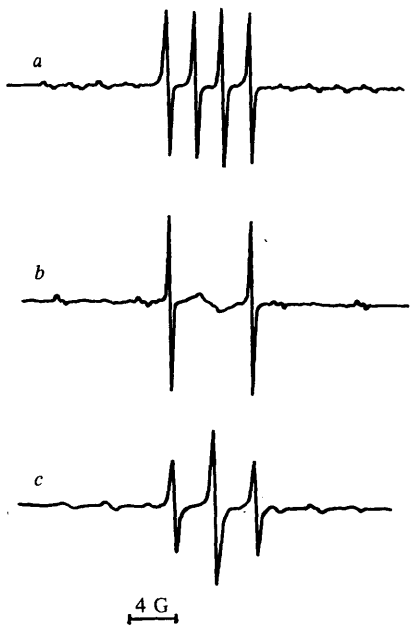
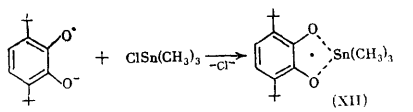


Figure 13. The EPR spectra of radical (XIII) in THF at different temperatures (°C): *a*) −70; *b*) 0; *c*) 110.

Radicals containing the trimethylstannyl group have been obtained by the reaction of 3,6-di-t-butyl-*o*-semiquinone radical-anions with chlorotrimethylstannane[62]:



The EPR spectrum of this radical is a triplet with a_H = 3.6 G due to the equivalent ring protons. In addition, the lines due to the paramagnetic tin isotopes are observed ($a_{^{117}Sn}$ = 12.8 G and $a_{^{119}Sn}$ = 13.3 G). Variation of temperature does not lead to a specific broadening of the spectral lines, which indicates either a stationary symmetrical disposition of the tin-containing group or its rapid migration (relative to the EPR time scale) between the oxygen atoms.

Stannotropic transitions, revealed by EPR spectra, have been observed in radical (XIII), obtained by the interaction of the semiquinone radical-anion with dichlorodimethylstannane[62]:

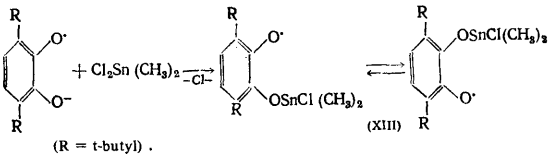


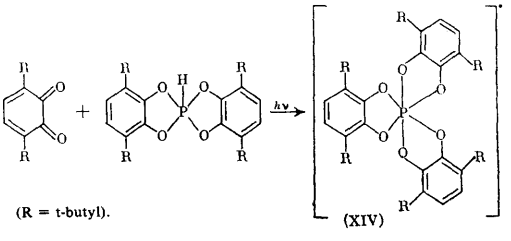
Fig. 13 shows that, as the temperature is reduced from 110° to −70°C, the EPR spectra of radical (XIII) reveal a transition from the triplet with a_H = 3.6 G, due to the HFI of the equivalent aromatic ring protons, to a doublet of doublets (a_H = 5.2 G, a_H = 2.6 G), which indicates the breakdown of the "equivalence" of the ring protons. An alternation of line widths, due to the intramolecular migration of the tin-containing fragment, is observed in the intermediate temperature range. The kinetic parameters of the tautomerism of radicals (VI), (XII), and (XIII) in THF are presented below:

Migrating radical	$\nu(20°)$, s^{-1}	$10^{-12}\nu_0$, s^{-1}	$E_{act} \pm 0.5$ kcal $mole^{-1}$
(VI) $-CH_3$	0	—	—
(XII) $-Sn(CH_3)_3$	10^9	—	—
(XIII) $-Sn(CH_3)_2Cl$	$9 \cdot 10^6$	50	9.1

The data presented permit a quantitative comparison of the migration frequencies of fragments containing Group IV elements. The increase of migration frequency on passing from carbon to tin [radicals (VI), (XII), and (XIII)] illustrates the decisive role of the coordination unsaturation of the central atom of the migrating fragment in tautomeric transitions.

3. Free Radicals with a Six-Coordinated Phosphorus Atom

The above examples constitute "two-well" tautomeric systems (migration of fragments between two oxygen atoms). We shall now examine more complex instances of degenerate tautomerism, where the free valence migrates between six or four oxygen atoms ("wandering" valence). Such radicals have been obtained as a result of the interaction of 3,6-di-t-butyl-*o*-quinone with tetra-t-butylspirophosphorane under the influence of ultraviolet radiation. This interaction can be represented as follows[63]:



At high temperatures the EPR spectrum of radical (XIV) is a doublet due to the interaction of the unpaired electron with the ^{31}P nucleus (a_P = 4.1 G). Each component of the doublet contains seven lines (a_H = 1.45 G), the intensity ratios of which indicate unambiguously the interaction of the unpaired electron with six "equivalent" ring protons (Fig. 14*a*). With decrease of temperature, the HFS components with the proton nuclear spin projections $M_I = \pm 2$, ± 1 are broadened (Figs. 14*b*, 14*c*, and 14*d*) and at fairly low temperatures (−80° C) a spectrum is recorded in which each component of the phosphorus doublet contains three lines (a_H = 4.35 G) (Fig. 15*e*) corresponding to the interaction of the unpaired electron with two equivalent protons in a single ring. The above changes in the spectra are fully reversible with respect to temperature; the constant for hyperfine interaction with the ring protons is smaller by a factor of three in the high-temperature spectra than in those at low temperatures (Fig. 14).

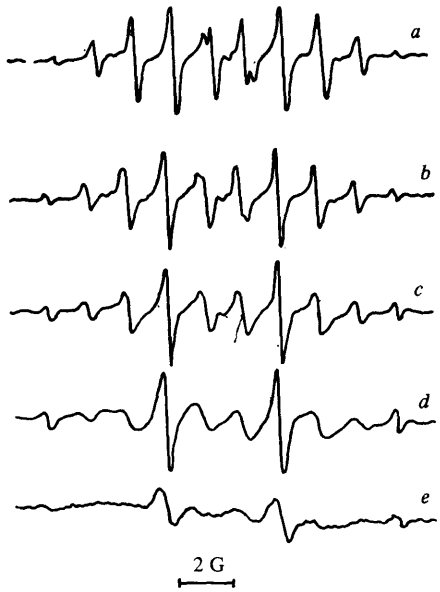
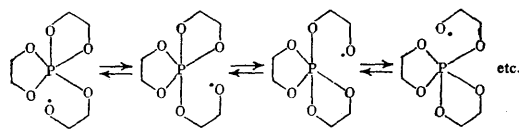


Figure 14. The EPR spectra of radical (XIV) in toluene at different temperatures (°C): *a*) 0; *b*) −20; *c*) −40; *d*) −60; *e*) −80.

In interpreting the results one must bear in mind that the high-temperature spectra indicate the presence of six equivalent protons in radical (XIV). Since a specific broadening of the components of the septet, indicating the occurrence of dynamic effects, is observed when the temperature is reduced, presumably the "equivalence" of the six protons at high temperatures is achieved as a result of rapid exchange of the free valence and a bond in the system:



The free valence then "runs round" all six oxygen atoms of the catechol ligands and, in terms of the EPR scale, the phosphorus atom has a coordination number of six.

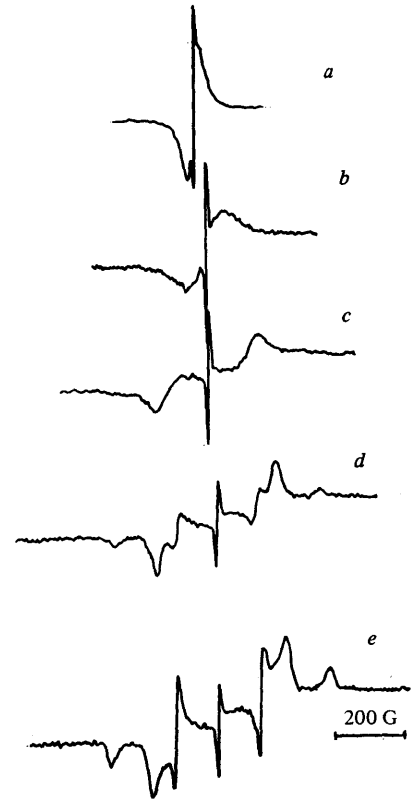
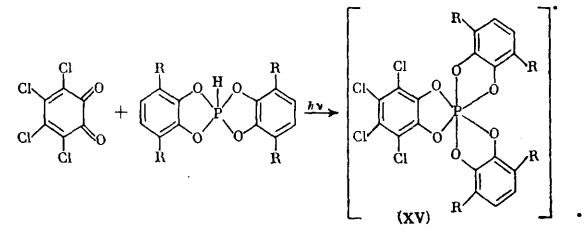


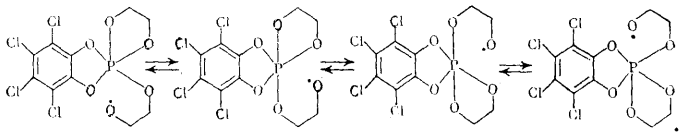
Figure 15. The EPR spectra of biradical (XVI) in toluene at different temperatures (°C): *a*) 0; *b*) −40; *c*) −80; *d*) −100; *e*) −130.

Analogous effects involving the "wandering" of the free valence have been obtained for radical (XV):



At high temperatures each component of the phosphorus doublet contains five lines owing to the four protons of the two 3,6-di-t-butylcatechol ligands, which indicates the exchange of the unpaired electron and a bond between these ligands. The delocalisation of the unpaired electron over the two catechol ligands makes the HFI constant for

the ring protons greater by a factor of 1.5 than in radical (XV) and indicates the absence of the exchange of the unpaired electron and a bond in the *o*-chloranil ligand:



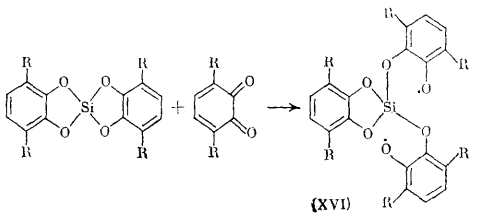
Analysis of line widths made it possible to estimate the energy parameters of the "wandering" of the free valence, the general expressions for which are as follows in the case of radicals (XIV) and (XV):

$$\nu_{XIV},\ (s^{-1}) = 3{,}4 \cdot 10^{12} \exp\left[-(4{,}3 \pm 0{,}5)/RT\right],$$
$$\nu_{XV},\ (s^{-1}) = 0{.}9 \cdot 10^{12} \exp\left[-(3{.}6 \pm 0{.}5)/RT\right].$$

At 20°C the frequencies of the "wandering" of the free valence in these radicals are similar and amount to 2×10^9 s^{-1}.

4. Free Radicals with a Six-Coordinated Silicon Atom

The effects associated with the intramolecular exchange of an electron and a bond in multiwell systems, which we have referred to as the "wandering" of the free valence, have been observed for free radicals with a six-coordinated silicon atom. Such radicals have been obtained by the interaction of silicon bis-3,6-di-t-butylcatecholate with 3,6-di-t-butyl-*o*-quinone, which leads to the formation of biradicals[64]:



(XVI)

The EPR spectra obtained for frozen solutions of these species are characteristic of biradical systems (Fig. 15) with an effective spin–spin interaction of two unpaired electrons, manifested by the presence of the zero splitting constants D and E. On raising the temperature, the spin–spin interaction is averaged out and the EPR spectrum of the liquid phase consists of a single broad line, which narrows on raising the temperature (Fig. 15). The line width between the points of maximum slope at 20°C is 25 G. Such a change in the spectra is characteristic of stable biradicals of the phenoxy-type and confirms the proposed structure of the species formed[23]. At half-field ($g = 4$) an intense absorption is observed (in frozen solutions), corresponding to a transition with $\Delta m = \pm 2$ and persisting down to −80°C.

Analysis of the main spectrum (Fig. 15*e*) gave the zero splitting parameters $D = 322$ G and $E = 24$ G. The non-zero value of E indicates the absence of axial symmetry in the unpaired electron distribution in biradical (XVI). The constant D characterises the average distance between the spins and, in terms of the point dipole approximation, is defined by the expression $D = g\beta r_{av}^{-3}$. One must bear in mind that the unpaired electrons are delocalised over the conjugated bond system of the catechol rings and, for small distances between the radical centres, comparable with the unpaired electron delocalisation regions, the point model may prove to be inapplicable to the estimation of distances between the interacting spins.

The parameter D depends greatly on r_{av}, so that one may assume that the main contribution to D comes from the spin density ρ_o at the oxygen atoms of biradical (XVI) capable of maximum mutual approach. The estimate of the distribution of spin density in the 3,6-di-t-butyl-2-hydroxyphenoxy-radical[65], whose structure is similar to that of the radical fragments of biradical (XVI), suggests that $\rho_o = 0.3$, so that $r_{av} = 3$ Å. If biradical (XVI) has a "quasi-octahedral" configuration owing to the coordination of the unpaired electrons to the vacant orbitals of silicon, then the univalent oxygen atoms may be either in the *cis*- or *trans*-positions relative to one another. The *trans*-positions for normal SiO bonds are separated by a distance of 3.3 Å. For coordinate bonds, these distances are apparently greater, and one may therefore assume that the distance $r = 3$ Å in biradical (XVI) corresponds to the *cis*-positions of the "univalent" oxygen atoms. This is confirmed by the absence of axial symmetry ($E \neq 0$) in the spectra of frozen solutions.

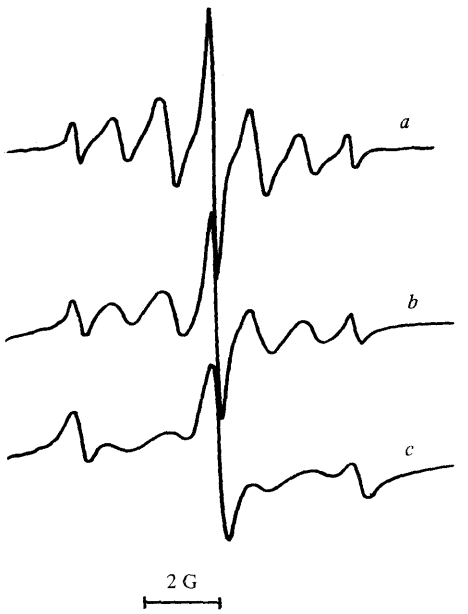
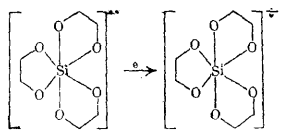


Figure 16. The EPR spectra of radical (XVII) in THF at different temperatures (°C): *a*) −40; *b*) −60; *c*) −80.

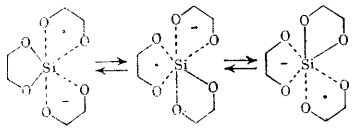
The main evidence for the structure of biradical (XVI) was the spectroscopic detection of the radical-anion (XVII), obtained by the electrochemical reduction of biradical (XVI):



(XVI) (XVII)

Fig. 16 presents the EPR spectrum of radical-anion (XVII) in THF, which consists at low temperatures (−80°C) of three lines due to the interaction of the unpaired electron with two protons in a single catechol ligand ($a_H = 3.75$ G).

With increase of temperature, additional broad lines appear in the spectrum, becoming narrower on further heating (Figs. 16*a* and 16*b*) and indicating the interaction of the unpaired electron with six "equivalent" protons and three catechol rings (a_H = 1.25 G). The above changes are fully reversible when the temperature is altered and indicate intramolecular processes. These reduce to the "wandering" of the free valence and the charge in accordance with the mechanism



The electronic structure of radical-anion (**XVII**) differs from that of the usual radical-anions obtained on reduction of neutral organic compounds. In the ion pairs formed by the latter compounds the motion of the cation is indissolubly linked to the synchronous redistribution of the charge and spin intensities of the unpaired electron over the system of conjugated bonds (for example in semiquinone radical-anions, see Section III). In ion pairs formed by radical-anion (**XVII**) the charge and spin densities are in principle separate and localised in different ligands. Under these conditions, the migration of the cation (and the redistribution of charge density) may take place to some extent independently of the exchange of the free valence and a bond, as can be seen from an examination of the "instantaneous" structures of ion pairs formed by radical-anion (**XVII**):

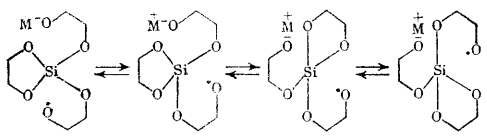


Table 2. The kinetic parameters of the interligand electron exchange in ion pairs comprising radical-anion (**XVII**).

Cation	Solvent	$10^{-4}\,\nu\,(20°)$, s^{-1}	$10^{11}\nu_0$, s^{-1}	$E_{act} \pm 0.5$ kcal mole^{-1}
TBA^+	THF	10^3	10	4.1
Na^+	THF + crown	$4\cdot10^2$	10	4.6
Na^+	THF	2.5	7.4	7.4
Na^+	DME	2.2	22	8.1
K^+	THF	1.8	1.5	6.6
K^+	DME	1.2	7	7.9
Li^+	THF	0.6	$3\cdot10^{-4}$	2.3
Li^+	DME	1.1	0.12	5.5

Note. TBA^+ is the tetrabutylammonium cation and crown stands for 18-crown-6 (0.01 M).

The characteristics of the structure of ion pairs formed by radical-anion (**XVII**) are clearly manifested in the variation of the frequency of the exchange (ν_{exch}) of the unpaired electron and a bond as a function of temperature, the nature of the cation, and the solvating properties of the medium (Table 2). In the free radical-anions (**XVII**) (tetrabutylammonium cation) and in alkali metal salts of radical-anion (**XVII**) in the presence of crown-ethers, which are powerful solvating agents, the kinetic parameters of the exchange are large and close to the values for radical (**XIV**) with a six-coordinated phosphorus atom, which has a similar structure but no negative charge. This supports the view that the rate-limiting stage of the interligand electron exchange in these species is the exchange of the free valence and a bond, i.e. an intramolecular radical substitution reaction.

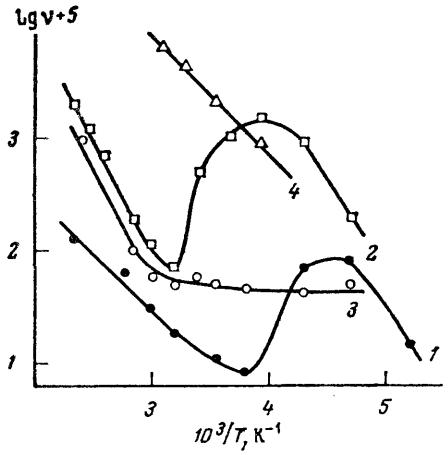


Figure 17. Dependence of the exchange frequency in radical-anion (**XVII**) on $1/T$ in DME for different cations: 1) Li^+; 2) Na^+; 3) K^+; 4) t-butylammonium.

Table 2 shows that in contact ion pairs formed by radical-anion (**XVII**) (alkali metal cations, weakly solvating solvents) ν_{exch} is appreciably lower and its temperature dependence in terms of Arrhenius coordinates is non-linear (Fig. 17). The rate-limiting stage of the exchange in contact ion pairs is the migration of a cation from ligand to ligand and a non-linear Arrhenius temperature dependence of ν_{exch} is due to the competition of two processes: the solvation of the cation by solvent molecules, responsible for the approach to the properties of free ions and the acceleration of the exchange frequency (low temperatures), and to the increase with temperature of the fraction of contact ion pairs in which the exchange frequency is much lower than in the solvated complexes. This competition in fact leads to the observed results: with increase of temperature, the exchange frequency initially falls and then increases again at very high temperatures (Fig. 18).

A characteristic feature of the exchange of the free valence and a bond in radical-anion (**XVII**) is the transition from the intraligand exchange immediately to the three-ligand exchange, bypassing the two-ligand exchange stage, which can be formally postulated on the basis of the above examination of the "instantaneous" structures of radical-anion (**XVII**). This can be explained by the fact that in contact ion pairs formed by radical-anion (**XVII**), where the unpaired electron is localised in one ligand, the cation tends to assume a symmetrical disposition relative to the other two catechol rings, determined by the coordination of the lone electron pairs of the oxygen atoms in the field of the cation (by analogy with crown-ethers). Such coordination prevents the involvement of the "vacant" ligand in the two-ligand exchange and creates conditions for the

involvement of all three ligands at once in the exchange process. This also explains why the migration of the cation is rate-limiting in the exchange of the free valence and a bond in contact ion pairs[66].

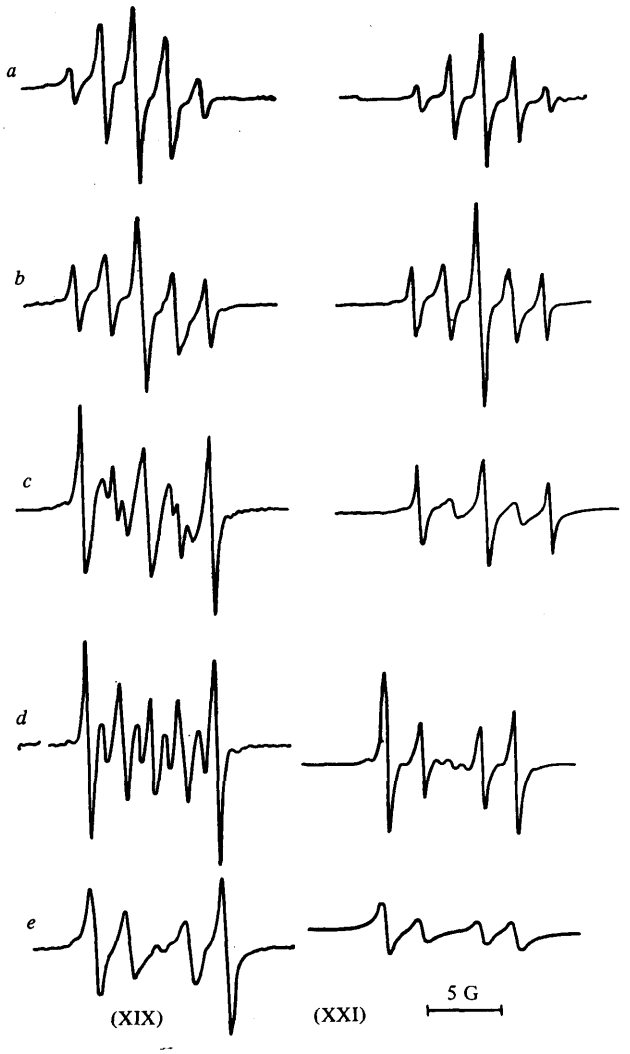
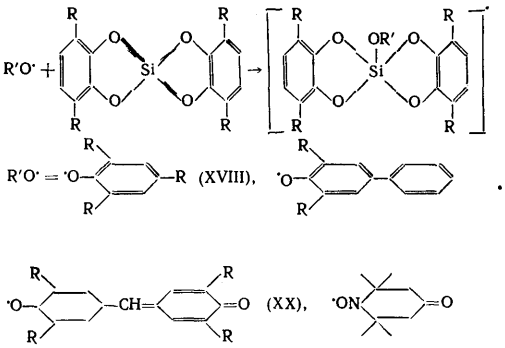


Figure 18. The EPR spectra of radicals (XIX) and (XXI) in pentane at different temperatures (°C): *a*) 80; *b*) 40; *c*) −40; *d*) −80; *e*) −110.

5. Free Radicals with a Five-Coordinated Silicon Atom

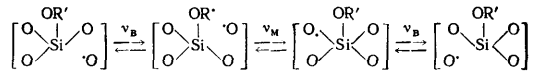
The two-ligand exchange of the unpaired electron and a bond has been investigated in detail in relation to free radicals with a five-coordinated silicon atom, obtained by the interaction of stable phenoxy- and iminoxy-radicals with silicon bis-(3,6-di-t-butylcatecholate) (SC)[67]:



The kinetic parameters of the exchange between the electron and a bond in radicals with a five-coordinated silicon atom in pentane are listed below:

Radical	$10^{-8}\nu(20°)$, s^{-1}	$10^{-11}\nu_0$, s^{-1}	$E_{act} \pm 0.5$, kcal mole^{-1}
(XVIII) — (XX)	22	44	4.5
(XXI)	4.5	4.2	4.1

At high temperatures (80° C) the spectra of these radicals consist of a quintet (Fig. 18), due to the interaction of the four "equivalent" protons of the two catechol rings (a_H = 2.19 G), the silicon atom has a coordination number of five in terms of the EPR time scale, and the unpaired electron "runs round" the four oxygen atoms in the two catechol rings with a high frequency ("wandering" valence):



In other words, the rapid exchange condition is fulfilled; ν_B and ν_M are the frequencies of the exchange of the unpaired electron and a bond within a single ligand and between ligands respectively.

It is striking that the exchange does not involve the Si–OR bond, where it is possible to specify formally a state corresponding to the initial reactants (RO· and SC). It has been shown for radical (XXI) that at high temperatures (in excess of 100° C) this state does exist, but it corresponds simply to the reverse dissociation of radical (XXI) and the EPR spectra show a decrease of the intensity of the (XXI) lines and the appearance of the spectrum of the initial iminoxy-radical. At lower temperatures the equilibrium is wholly displaced towards radical (XXI) and the exchange takes place only between the catechol ligands and within them (the quintet due to the four "equivalent" protons of the two catechol rings). The alternative hypothesis of the possible ionic character of the Si–OR bond is unlikely, because the ultraviolet spectra of radicals (XVIII)–(XXI) obtained lack bands characteristic of the RO^- anion.

With decrease of temperature, the components of the quintet with $M_I = 0, \pm 1$, are broadened, which indicates inhibition of the exchange (Figs. 18*b* and 18*c*). At low temperatures (−110° C) the spectrum consists of a doublet (a_4^H = 6.37 G), each component of which is split into two lines (a_5^H = 2.37 G) (Fig. 18*e*) and corresponds to the structure with the localisation of the unpaired electron at one oxygen atom of the catechol ligand (slow exchange condition fulfilled)[67]. The HFI constants were assigned on the basis of the generally accepted ideas, according to which the maximum HFI is due to the proton in the *para*-position relative to the univalent oxygen atom.

The kinetic parameters of the exchange of the unpaired electron and a bond were estimated from the broadening of the central component of the quintet (relative to the extreme components) and reflect the change in the exchange frequency as a function of the nature of the added radical and the solvent. In pentane the frequencies and the energy barriers estimated in this way are similar for all radicals (see above).

In the intermediate exchange frequency range ($\nu_B, \nu_M \simeq \gamma_e \Delta a$) the alternation of line widths in the EPR spectra of radicals (XVIII)–(XXI) has its characteristic features. Firstly, the central component ($M_I = 0$) and lines with $M_I = \pm 1$ in the quintet are broadened non-uniformly and their intensity ratios change from 4 : 6 : 4 (high temperatures) to 1 : 2 : 1 (when the temperature is reduced—Figs. 18*a*, 18*b*, and 18*c*), and in certain cases even as far as 1 : 3 : 1.[67] On further reduction of temperature, the central component becomes less intense than the lateral ones ($M_I = \pm 1$) and additional lines appear, vanishing as a result of a further reduction of temperature accompanied by the formation of a doublet of doublets (Figs. 18*c*, 18*d*, and 18*e*).

Before analysing these features, it is necessary to examine the individual contributions to the line widths taking into account the intra- and inter-ligand exchange processes as the intermediate stages in the inhibition of the overall exchange in the course of the localisation of the unpaired electron at one of the oxygen atoms (Fig. 19). From this standpoint, the radicals investigated may be regarded as "four-well" systems with potential energy minima for each of the four oxygen atoms. This system can be formally divided into two types of "two-well" subsystems, in the first of which the exchange of the electron and a bond takes place in a single ligand [intraligand exchange (ν_B)]. For this exchange, the EPR spectrum should consist of a triplet due to the interaction of the unpaired electron with the two "equivalent" protons of a single catechol ring; the HFI constant for this triplet is equal to half the sum of the HFI constants for the limiting structure (Fig. 19). The second type involves exchange between the oxygen atoms of different ligands [interligand exchange (ν_M)]. This case should give rise to a spectrum consisting of a triplet due to the presence of two *para*-protons (the 4-position relative to the univalent oxygen atom); its HFI constant is equal to half the HFI constant for the *para*-proton in the limiting structure. Each component of this triplet contains three lines due to the *meta*-protons (the 5-positions in the two-ligands) with an HFI constant equal to half the constant for the *meta*-proton in the limiting structure (Fig. 19).

One can imagine that the inhibition of the overall exchange (the conversion of the quintet into a doublet of doublets) proceeds via preliminary stages involving complete inhibition of one of the types of migration: type I with $\nu_B \gg \nu_M$ and type II with $\nu_B \ll \nu_M$. In these cases the spectrum should vary in accordance with the schemes in Fig. 19 with the intermediate formation of a triplet and a triplet of triplets respectively. However, the experimental spectra are complex (Fig. 18), which necessitates the hypothesis that both types of migration occur simultaneously in radicals (XVIII)–(XXI).

To test this hypothesis, the contributions to the width of the quintet $\Delta(T_2^{-1})$ were calculated for the two cases considered[67]. Evidently, whereas the broadening of the central component of the triplet is the same for both types of inhibition of the exchange, for the components with $M_I = \pm 1$ the broadening is different in each case. We calculated these contributions using the HFI constants for the limiting structures of the radicals investigated. Table 3 (type I) shows that four lines of the central component make a minimal contribution (16 G) compared with the lines having $M_I = \pm 1$ (35 G). This explains the non-uniform broadening of the components, mentioned above. The sharp decrease of the intensity of the central component on further reduction of temperature may be due to the predominance of the type II inhibition ($\nu_B \ll \nu_M$). Indeed in this case the minimal contribution to the broadening comes from the lines with $M_I = \pm 1$ (9.6 G) compared with the central component (16 G). This is also supported by the appearance of additional lines (the formation of a nine-line spectrum) on further reduction of temperature (Figs. 18*c* and 18*d*), which may be attributed to the intermediate formation of a triplet of triplets (cf the scheme in Fig. 19). The discrepancy between the intensities may be due to the non-rigorous fulfilment of the rapid exchange condition for the individual components at a particular exchange frequency (different contributions to the width) and also to the presence of an intermediate spectrum of the exchange inhibition type (a triplet, Fig. 19).

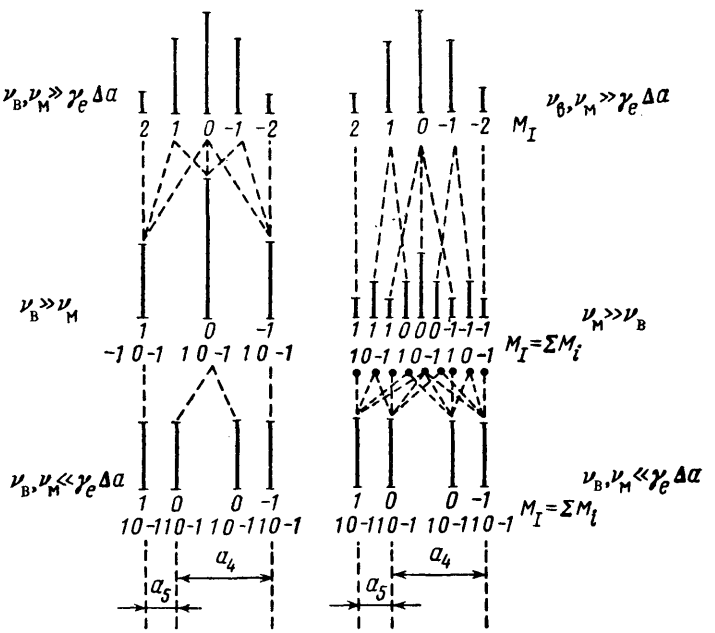
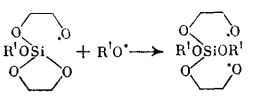


Figure 19. Schematic representation of the spectra of radicals (XVIII)–(XXI) under the conditions of the inhibition of the interligand exchange (type I) and the intraligand exchange (type II).

The increase of the thermodynamic stability of radicals (XVIII)–(XXI) after their formation suggests that they can combine with yet another initial radical to form the corresponding biradicals. Such species are produced when SC is made to react with an excess of the initial radicals:



Under these conditions, the EPR spectra shows signals characteristic of biradical systems; analysis of the spectrum makes it possible to determine the zero splitting constants for the biradicals ($D = 335 \pm 8$ G, $E = 21 \pm 2$ G). Estimates of the distances between the unpaired electrons yield 2.9 Å, which indicates the coordination of the unpaired electrons to the vacant orbitals of silicon. In frozen solutions signals at half-field ($g = 4$) are also recorded and at the usual temperatures signals in the form of single broad lines have been observed.

Table 3. The contributions $\Delta(T_2^{-1})$ to the width of the components of the quintet in the spectra of radicals (XVIII)–(XXI) under conditions of the inhibition of the exchange of the unpaired electron and a bond. (The numerical contributions were obtained with the following HFI constants: $a_4^H = 6.37$ G and $a_5^H = 2.37$ G).

Fast exchange				Intermediate exchange			
				type I exchange, $\nu_B \gg \nu_M$		type II exchange, $\nu_B \ll \nu_M$	
M_I	degeneracy	$M_I = \Sigma M_i$	degeneracy	$\Delta(T_2^{-1})$	$\Delta(T_2^{-1})$, G^2	$\Delta(T_2^{-1})$	$\Delta(T_2^{-1})$, G^2
±2	1	±1, ±1	1	0	0	0	0
±1	4	±1, 0	2	$^1/_4(a_4+a_5)^2+(a_4-a_5)^2$	35	$^1/_4(a_4-a_5)^2+a_5^2$	9.6
		0, ±1	2	$^1/_4(a_4+a_5)^2+(a_4-a_5)^2$	35	$^1/_4(a_4-a_5)^2+a_4^2$	44.5
0	6	0, 0	2	$(a_4+a_5)^2$	76.5	$(a_4+a_5)^2$	76.5
		±1, ±1	4	$(a_4-a_5)^2$	16	$(a_4-a_5)^2$	16

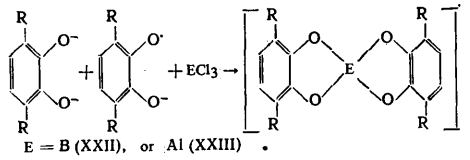
Table 4. The spectroscopic parameters of radicals (XXII) and (XXIII).

Radical	Element (E)	Content,%	I	ν_μ^*	a_E, G	a_H, G	
						slow exchange	fast exchange
(XXII)	^{11}B	81.3	3/2	29	2.5	4.5	2.25
	^{10}B	18.8	3	9.7	0.83	4.5	—
(XXIII)	^{27}Al	100	5/2	23.5	2.58	4.0	2.0

*The magnetic moments are expressed in terms of the NMR frequencies for a constant field of 21.14 kG.

6. Free Radicals with Four-Coordinated Boron and Aluminium Atoms

The effects associated with the "wandering" of the free valence have been observed also for radicals with four-coordinated boron and aluminium atoms, obtained as a result of the following reaction[68]:



E = B (XXII), or Al (XXIII).

The EPR spectrum of the boron-containing radical (XXII) is a quartet (Fig. 20), due to the interaction of the unpaired electron with the main paramagnetic ^{11}B isotope (Table 4).

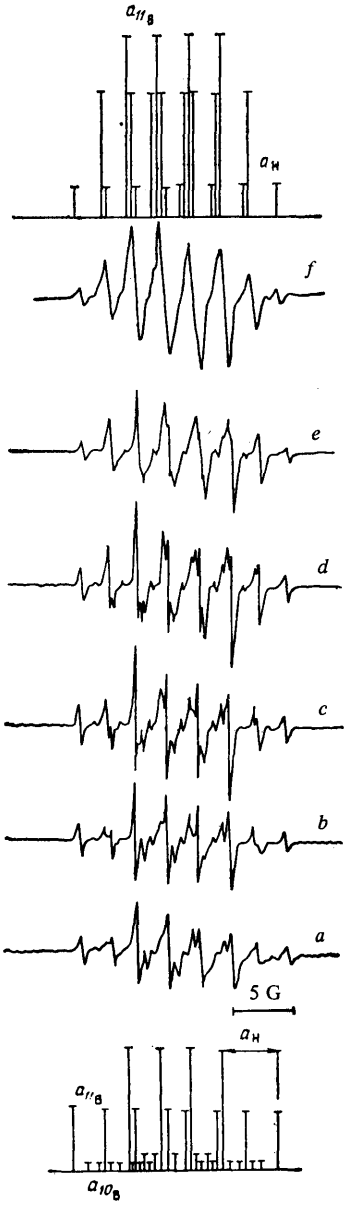


Figure 20. The EPR spectra of radicals (XXII) in THF at different temperatures (°C): *a*) −100; *b*) −80; *c*) −60; *d*) −40; *e*) −20; *f*) 20; data obtained from the reconstruction of the spectra corresponding to high and low temperatures and obtained with the HFI constants listed in Table 4.

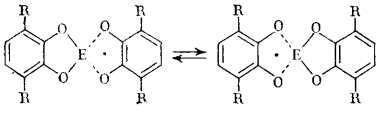
Each component of this quartet consists at low temperatures (−100°C) of a triplet (1 : 2 : 1) due to two protons of a single catechol ring (Fig. 20*a*). In addition, lines due to the ^{10}B isotope can be observed in the spectra at low temperatures. The ratios of the constants for the interaction

of the unpaired electron with paramagnetic boron isotopes ($a_{^{11}B}/a_{^{10}B} = 3$) and the intensity ratio of the corresponding lines ($I_{^{11}B}/I_{^{10}B} = 7.5$) agree satisfactorily with the values calculated theoretically on the basis of the analysis of the magnetic moments of the nuclei and the natural abundances of the two isotopes (3 and 7.6 respectively).

When the specimen is heated, additional broad lines, narrowing on further increase of temperature (Figs. 20*b*, 20*c*, and 20*d*), are observed. At 20°C and above, each component of the boron quartet is transformed into a quintet with binomial intensity ratios (Fig. 20*e*) due to the interaction of the unpaired electron with the four equivalent protons of the two catechol rings. The changes in the spectra are fully reversible with respect to temperature and the HFI constant for the quintet is smaller by a factor of two than for the triplet at low temperatures.

Analogous changes occur in the EPR spectra of radical (XXIII), which has a central aluminium atom. Its spectra are illustrated in Fig. 21 and confirm the proposed structure. Six lines are due to the ^{27}Al nucleus (Table 4) and each component of the sextet consists of a triplet (low temperatures, Fig. 21*a*) or a quintet (high temperatures, Fig. 21*e*) due to the interaction of the unpaired electron with the protons of one or two catechol rings respectively.

The observed dynamic effects in the EPR spectra of radicals (XXII) and (XXIII) indicate rapid exchange of the free valence and a bond in these radicals:



At high temperatures the free valence "runs round" the four oxygen atoms and the B and Al atoms have tetrahedral configurations in terms of the EPR time scale. As for the free radicals with a six-coordinated phosphorus atom, the barriers to the transition within a single ligand are overcome at low temperatures and the unpaired electron interacts with the protons of a single ring[68].

Analysis of line widths made it possible to estimate the kinetic parameters of the "wandering" of the free valence, the general expressions for which are of the following form in the case of radicals (XXII) and (XXIII):

$$\nu_{XXII}, (s^{-1}) = 1{,}8 \cdot 10^{13} \exp[-(4200 \pm 300)/RT],$$

$$\nu_{XXIII}, (s^{-1}) = 3.2 \cdot 10^{11} \exp[-(3000 \pm 300)/RT].$$

At 20°C we have $\nu_{XXII} = 2 \times 10^9\ s^{-1}$ and $\nu_{XXIII} = 1.25 \times 10^{10}\ s^{-1}$.

Thus the spectroscopic data obtained constitute convincing evidence in support of the structures proposed for the radicals under consideration and illustrate the existence in the latter of a "wandering" valence in the presence of four-coordinated boron and aluminium atoms. The differences between the frequencies and the exchange of the free valence and a bond in these radicals are apparently due to the difference between the types of element–oxygen bonds.

The processes associated with degenerate tautomerism considered above can serve, depending on the type of migrating species, as models of heterolytic (cationotropism) and homolytic (intramolecular radical substitution) reactions. The study of the ion pairs formed by radical-anions, cationotropic processes, and the solvation of ions has greatly extended our ideas about the occurrence of ionic processes in organic solvents.

The conclusion that the mobility of the cation plays an important role in intramolecular electron transfer processes we believe to have a more general importance, going outside the limits of the chemistry of radical-anions. The idea that certain reactions proceed via an electron transfer stage is being developed at the present time[69,70]. In those cases where compounds containing alkali or other metal cations, for example, organometallic compounds, alkoxides, radical-anions, etc. serve as electron donors it is necessary to take into account the role of dissociative processes, without which it is impossible to describe correctly the electron transfer processes.

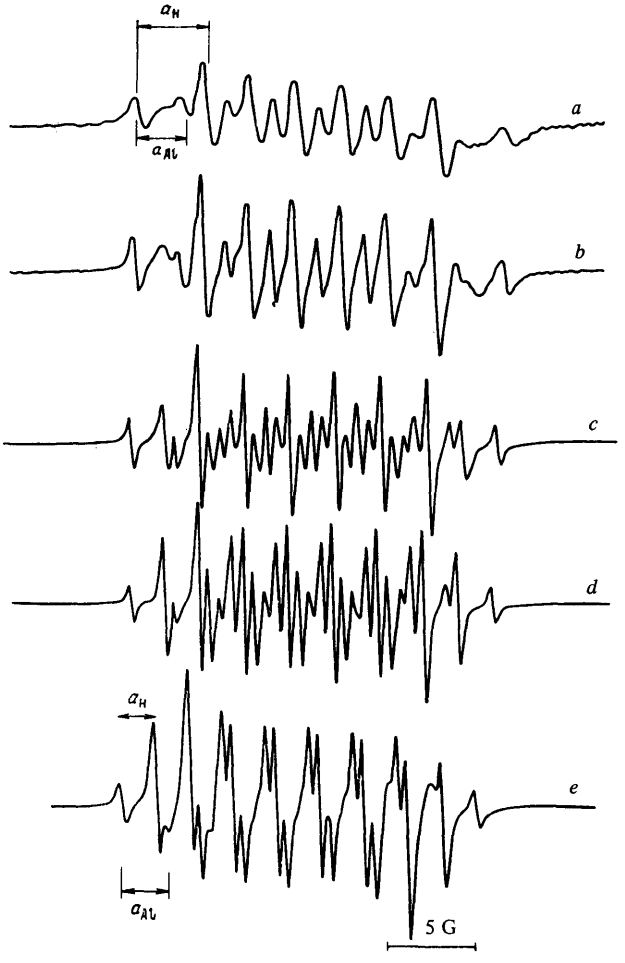


Figure 21. The EPR spectra of radical (XXIII) in THF at different temperatures (°C): *a*) −110; *b*) −100; *c*) −80; *d*) −40; *e*) 0.

The above examples of the tautomerism of radicals illustrate a type of tautomeric transformation new to organic chemistry, which constitute in essence intramolecular radical substitution reactions and permits certain generalisations concerning factors influencing the frequency

of the transfer of the migrating fragments. In the simplest instances (migration of hydrogen and deuterium) it is evident that the formation of an intramolecular hydrogen bond intensifies the tendency of these atoms to assume a symmetrical disposition relative to the oxygen atoms of the catechol ring (the difference between the lengths of the normal and hydrogen bonds for the planar disposition of the O...HO fragment is only 0.3 Å[57]). The introduction of solvents capable of forming hydrogen bonds inhibits the migration of hydrogen owing to the competitive effects involving the formation of intermolecular hydrogen bonds by these solvents with the proton of the hydroxy-group.

In all the remaining cases considered the electron deficiency at the central atom of the migrating fragment promotes the coordination of the "univalent" oxygen to the vacant orbitals of this atom, which leads to high frequencies of the tautomeric transitions observed by the EPR method (10^6–10^{10} s^{-1}).

The tautomeric transformations in free radicals with four-, five-, and six-coordinated atoms of Group III, IV, and V elements ("wandering" valence) constitute in essence a new type of delocalisation of the unpaired electron namely delocalisation with bond dissociation. The data obtained suggest that analogous effects should be observed in the corresponding diamagnetic anions and should be associated with the "wandering" of the charge at a frequency which depends significantly on the state of the ion pairs involving these anions.

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