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TAUTOMERISM IN SILICON-CONTAINING FREE RADICALS

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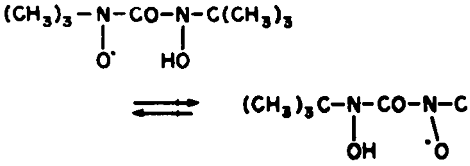
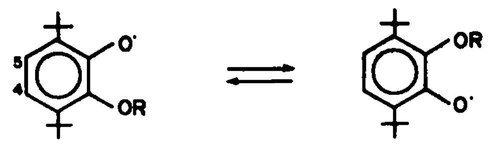
Abstract—Silicon-containing free radicals with 3,6-di-t-butylpyrocatechinic ligands have been investigated by ESR method. Intramolecular migrations of free valence and bond was found for these systems. It was considered in terms of intramolecular radical substitution.

Tautomerism of free radicals is intramolecular migration of organic and organoelemental fragments between equivalent and nonequivalent positions in radicals accompanied by synchronous redistribution of unpaired electron density in these species. In neutral free radicals this phenomenon may be formally considered as intramolecular radical substitution, as a result of which exchange between free valence and bond may occur. For instance, in the simplest case of hydrogentropy, first observed by Aurich and Stork:[1]



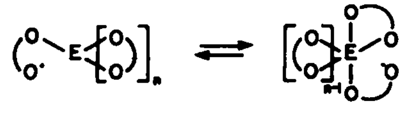
$$(CH_3)_3-\underset{O^{\bullet}}{\underset{|}{N}}-CO-\underset{HO}{\underset{|}{N}}-C(CH_3)_3 \rightleftharpoons (CH_3)_3C-\underset{OH}{\underset{|}{N}}-CO-\underset{{}^{\bullet}O}{\underset{\backslash}{N}}-C(CH_3)_3$$

Similar processes of intramolecular transfer of hydrogen, deuterium,[2] acylic groups,[3] fragments containing tin,[4] phosphorus,[5-7] boron and aluminum[8] and arsenic[9] have been recently studied in our laboratories for free radicals containing 3,6-di-t-butylpyrocatechinic ligands



R is an organoelemental group.

In the presence of several such ligands interligand exchange of the unpaired electron and bond was established which was designated "wandering" of free valence:[5-9]



 is the 3,6-di-t-butylpyrocatechinic ligand, E—P, As, B, Al.

The use of 3,6-di-t-butylpyrocatechinic ligand has two main advantages: firstly, the presence of bulky t-Bu groups in 3,6 positions of the pyrocatechinic ligand sharply increases the kinetic stability of the radicals and makes it possible to employ usual methods of ESR recording over a wide temperature range; secondly, the shape of the spectrum is significantly simplified: only interaction of the unpaired electron with ring protons in 4- and 5-positions is displayed. This enables examination of spectral features of the radicals in greater detail.

Results of ESR studies of such radicals containing organosilicon groups are summarized in this work. We recorded a large number of ESR spectra of organosilicon free radicals, analysis of which revealed various types of tautomeric conversions. We investigated migration of the organosilicon fragment between two O atoms of the free radical ligand, exchange of unpaired electron and bond between 4 and 6 O atoms in radicals, biradicals and anion-radicals (AR) with penta- and hexa- coordinated Si atoms.

The use of the ESR method is based on the effect of linewidth alternation in the hyperfine structure (HFS), typical of various intramolecular conversions in radicals (including tautomeric) which are accompanied by variation of hyperfine interaction (HFI) constants. Analysis of ESR linewidths permits quantitative study of the kinetics of conversions with times of 10^{-6}–10^{-10} sec. The physical meaning of linewidth alternation is that, as a result of molecular restructuring in the radical, HFI constants of certain nuclei vary in antiphase between two fixed values, for example, $a_1 = A$, $a_2 = B$ and $a_1 = B$, $a_2 = A$. This effect is revealed in certain HFS components exchanging their positions in the spectrum, the shape of which is determined to a considerable extent by kinetic parameters of exchange. The theory relating broadening of HFS lines with rates of exchange processes is given in Refs. 10–14. The chief results may be reduced to consideration of two cases.

Rapid exchange, when the rates of exchange processes are so fast that the spectra of individual forms are not observed and only averaged spectra are recorded. The shape of these spectra depends on the fluctuation in HFI constants on transition from one form into another and on the relative concentrations of these forms. The expression relating the frequency of intramolecular exchange (ν_{exch}) with line broadening caused by this exchange (ΔT_2^{-1}) may be written as

$$\Delta T_2^{-1} = \frac{\alpha(1-\alpha)\gamma_e(\Delta a)^2}{\nu_1+\nu_{-1}} \qquad (1)$$

where α and $(1-\alpha)$ are the molar fractions of exchanging inequivalent forms of the radical, ν_1 and ν_{-1} are the transition rates, γ_e is the gyromagnetic ratio for an electron and Δa is the distance between exchanging lines. For degenerate intramolecular transitions (1) takes the form

$$\Delta T_2^{-1} = \frac{\gamma_e(\Delta a)^2}{8\nu_{exc}} \qquad (2)$$

where

$$\nu_{exc} = \nu_1 = \nu_{-1}.$$

In the case of rapid exchange the lines are not broadened and the shape of the spectrum is determined only by the molar fractions of the forms.

In conditions of the so-called slow exchange, when the ESR spectrum corresponds to individual forms of the radical (in the degenerate case to one of the equivalent forms), the relationship between ν_{ex} and ΔT_2^{-1} is given by the simple expression

$$\Delta T_2^{-1} = \frac{\nu_{ex}}{2\gamma_e} \qquad (3)$$

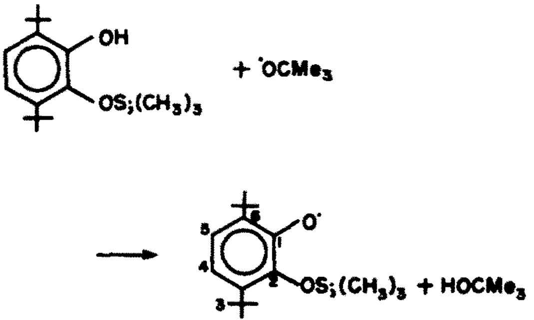
and ν_{ex} is determined directly from the linewidth.

In all cases considered in this work tautomerism is degenerate and the kinetic parameters of the process are determined from (2) and (3).

1. *Silylotropy of* 3,6-*di-t-butyl-2-trimethylsiloxyphenoxyl* ("two-hole" system)

3,6-di-t-butyl-2-trimethylsiloxyphenoxyl (I) was obtained by interaction of the initial phenol with di-t-butyl peroxide under UV irradiation directly in the ESR resonator[15]

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2\,Me_3CO^{\cdot}$$



(I)

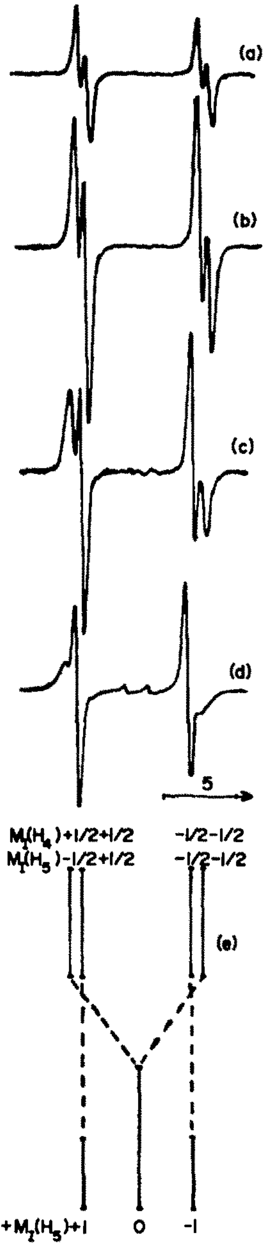
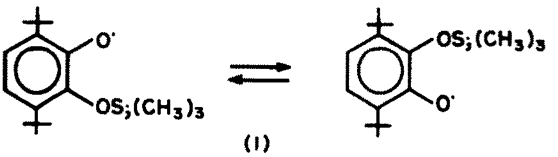


Fig. 1. ESR spectra of radical (I) in toluene: a—0°; b—20°; c—40°; d—60°.

The ESR spectrum of I in toluene is shown in Fig. 1. At 0° and below the main doublet is caused by interaction of the unpaired electron with the proton in position 4 ($a_H^4 = -8.4$ Oe); numbering of the ring positions of ligands is given in the formula of radical I.

Each component of this doublet consists of two lines due to the proton in position 5 ($a_H^5 = 0.62$ Oe). This interpretation of the spectrum completely conforms with the distribution of spin density typical of phenoxyl radicals,[13,16] according to which maximal positive density is in position 4 to the univalent O atom.

Increase of temperature leads to broadening of the outer lines (Fig. 1b,c,d) which is reversible. This broadening is due to migration of the trimethylsilyl group between O atoms of the pyrocatechinic ligand


(1)

In the temperature range studied the broadening lines are not displaced and slow exchange is realized. Under conditions of rapid exchange, which were not realized in our experiments, the ESR spectrum should comprise a triplet on account of the interaction of unpaired electron with "equivalent" ring protons with HFI constant equal to the half-sum of HFI constants in the limiting structure $a_H = (a_H^4 + a_H^5)/2$ (Fig. 1f), since the spin density in positions 4 and 5 have different signs in radical 1. The latter follows from broadening of the outer components of the spectrum and from the distribution of spin density of phenoxyl radicals.[13,16] Lines with the same projections of nuclear spins $M_I(\pm 1/2, \pm 1/2)$ do not change their position because the total magnetic field created by these nuclei is determined by the sum of HFI constants. Lines with opposite projections of nuclear spins $M_I(\pm 1/2, \mp 1/2)$ should transfer to the line with $M_I(0)$. This corresponds to rapid exchange since these lines exchange their positions as a result of migration of the trimethylsilyl group (the total magnetic field in this case is determined by the difference of HFI constants which changes sign during mutual transitions of constants a_H^4 and a_H^5).

The frequency of exchange was estimated from (2). Kinetic parameters of migration of some fragments containing Group IVA elements in radicals of similar structure are given in Table 1. The absence of Me migration in 3,6-di-t-butyl-2-methoxyphenoxyl(II) is apparently connected with saturation of the tetrahedral C atom of the Me group and, consequently, the impossibility of its coordination with univalent O atom. Carbotropic transitions were recorded in 3,6-di-t-butyl-2-acyloxyphenoxyls(III),[3] in which the electron deficiency on CO carbon enhances coordination of univalent oxygen. This is confirmed by positive acidic catalysis of acylotropy, which is realized through the protonated form of the CO group with increased electron deficiency.[17]

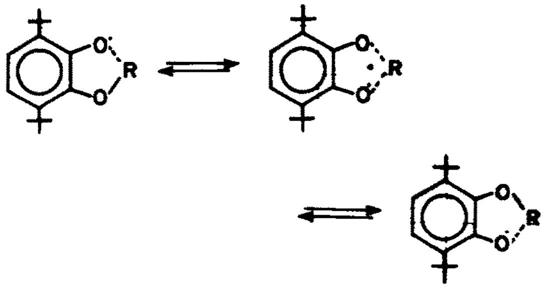
Table 1. Kinetic parameters of migration of fragments containing Group IVA elements

N	R	$\nu_{ex}(20°)s^{-1}$	$\nu_0 s^{-1}$	$E_{act} \pm 1.0$ (kcal/mole)
I	$Si(CH_3)_3$	2.5×10^6	1.6×10^{13}	9.3
II	CH_3	$\ll 10^4$	—	—
III	$COCH_3$	$\sim 10^4$	9×10^{12}	11.4
IV	$Sn(CH_3)_3$	$\gg 10^9$	—	—

The presence of vacant d-orbitals at the Si atom promotes such coordination and accelerates migration of the corresponding fragment.

Considerable coordination unsaturation of the Sn atom leads to migration of the trimethylstannyl moiety(IV) with frequencies higher than the characteristic time of ESR (Table 1).[4,15]

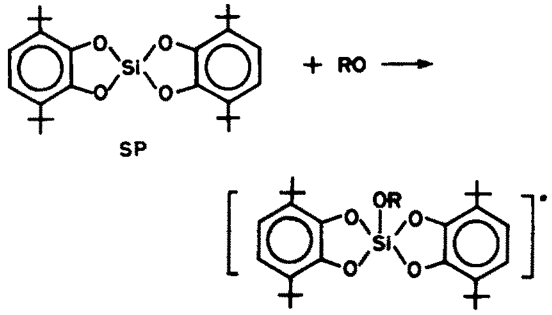
Hence, from the data obtained it may be concluded that coordination of univalent oxygen to the central atom of the migrating moiety creates preconditions for stabilization of the transition state, typical of radical substitution reactions and tautomeric processes:



These reactions should be classified as radical substitution reactions of the synchronous type,[18] since structures with localization of the unpaired electron on the central atom of the migrating fragment are not observed experimentally, and the unpaired electron is practically completely localized in the pyrocatechinic ligand. The latter follows from the similarity of spin density distributions in these radicals and in semiquinone anion-radicals of similar structure.[19,20]

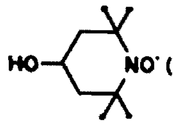
2. *Free radicals with penta-coordinated silicon* ("four-hole" systems)

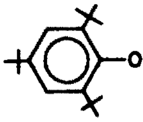
In the preceding section we studied radicals in which exchange of free valence and bond occurs between two O atoms of the same pyrocatechnic ligand. In this section we shall examine more complex cases of tautomerism when exchange involves 4 O atoms of two ligands. Preparation of such radicals is based on the weakness of the SiO bond in silicon bis-(3,3′,6,6′-tetra-t-butyl) pyrocatechate (SP) which easily ruptures under the effect of various reagents.[21] For example SP readily reacts with stable radicals forming radicals with penta-coordinated silicon (radicals V–VIII, Table 2):[22]

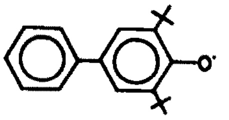


where

RO' –


(V)


(VI)


(VII)

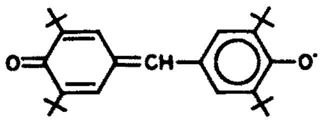
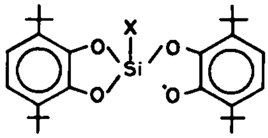

(VIII)

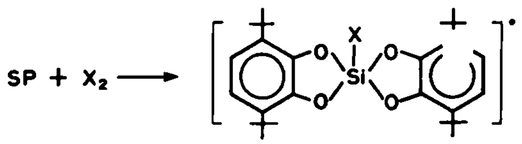
Table 2. Kinetic parameters of exchange between free valence and bond in radicals with pentacoordinated silicon in pentane



N	X	$\nu_{ex}(20°)c^{-1} \times 10^{-8}$	$\nu_0 c^{-1} \times 10^{-12}$	$E_{act} \pm 0.5$ (kcal/mole)
V	2,2,6,6-tetramethyl-4-hydroxypiperidine-1-hydroxyl	10	2.5	4.6
VI	2,4,6-tri-t-butylphenoxyl	0.57†	2.3	6.2
VII	2,6-di-t-butyl-4-phenylphenoxyl			
VIII	halvinoxyl			
IX	Cl	15	1.5	4.0
X	Br	3.1	28	6.7
XI	I	6.8	61	6.7
XII	F	400	2	2.3
XIII	2,6-di-t-butyl-4-hydroxyphenoxyl	10	2.5	4.6
XIV	2,3,5,6-tetramethyl-4-hydroxyphenoxyl	10	2.5	4.6
XV	3,5-di-t-butyl-2-hydroxyphenoxyl	12 1.1†	0.56 500	3.6 9.3 ± 3.0
XVI	3,6-di-t-butyl-2-hydroxyphenoxyl	2.7	0.68	4.6
XVII	$(CH_3)_3CO$	45 2.7†	4.3 6.8	4.0 6.0
XVIII	CH_3COO	8.0	80	6.7

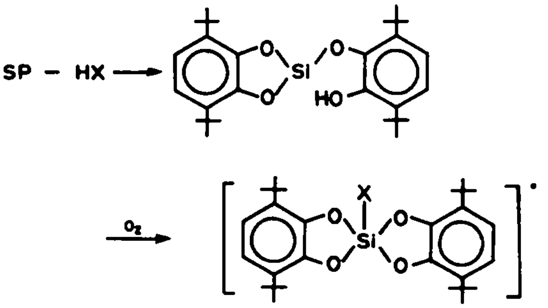
†Kinetic parameters obtained in vaseline oil.

In interaction with SP halogens are attached to the Si atom forming similar radical (IX–XI, Table 2):



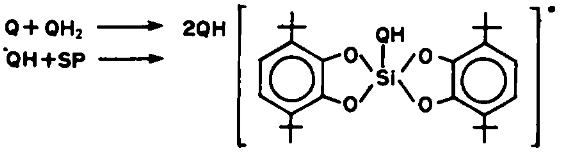
where X–Cl(IX), Br(X), I(XI).

Exactly identical spectra were obtained in interaction of SP with hydrogen halides. Presumably, the SiO bond is cleaved with formation of phenol, subsequent oxidation of which by atmospheric oxygen leads to similar products:

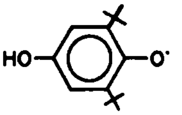


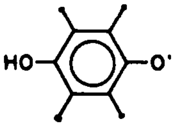
where X–F, Cl, Br, I.

Formation of such radicals is due to interaction of semiquinone radicals (in equilibrium with the initial quinone and hydroquinone[23]) with SP:



where $\dot{Q}$H


(XIII)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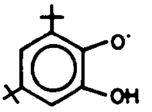
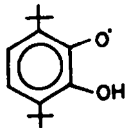
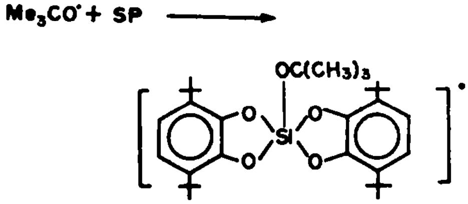

(XV)

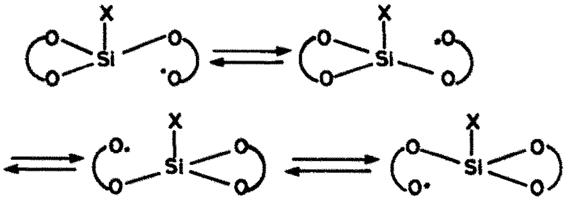

(XVI)

Interaction of t-butoxyl radicals formed by decomposition of di-t-butyl peroxide with excess of SP results in formation of the same type of radicals (XVII):



(XVII)

The ESR spectra of all these radicals (V–XVIII, Table 2) at high temperatures (above 40°) are represented by multiplets with binominal intensity ratio (1:4:6:4:1) determined by the four "equivalent" protons of two pyrocatechninic ligands (a_H 2.13 Oe, Fig. 2a).† The Si atom has a coordination number of five in the ESR time scale and the unpaired electron migrates with high frequency between four O atoms:



 is the 3,6-di-t-butylpyrocatechinic ligand. In other words the condition of rapid exchange is fulfilled $\nu_{intra}\cdot\nu_{inter} \gg \gamma_e\Delta a$[10] where ν_{intra} and ν_{inter} are the frequencies of intra and interligand exchange respectively.

At lower temperatures the three central components of the quintet with $M_I = 0, \pm 1$ are broadened indicating retardation of exchange (Fig. 2b,c). At low temperatures (−100°) the ESR spectra are characterized by the presence of a doublet ($a_H{}^4$ 6.37 Oe) each component of which is splitted into two lines ($a_H{}^5$ 2.37 Oe) and corresponds to the structure with localization of the unpaired electron on an O atom (conditions of slow exchange are fulfilled, $\nu_{intra}\cdot\nu_{inter} \ll \gamma_e\Delta a$) (Fig. 2e).

In the intermediate frequency range ($\nu_{intra}\cdot\nu_{inter} \sim \gamma_e\Delta a$) alternation of linewidths have several common features. The central component ($M_I = 0$) and lines with $M_I = \pm 1$ of the quintet broaden differently on decrease of temperature. This is exhibited in change of their relative intensities from 4:6:4 (high temperatures) to 1:2:1 (at low temperatures) and in some cases to 1:3:1. At lower temperature the central component becomes weaker than the side components (with $M_I = \pm 1$) and the spectra display nine lines (Fig. 2d). The latter is converted into a doublet of doublets on further decrease of temperature (−100°, Fig. 2e).

Before analyzing these features let us first examine the radicals as "four-hole" systems with minimum of potential energy on each of the four O atoms. Such a system may be divided into two types of "two-hole" subsystems. The first type of exchange of electron and bond is spectrally realized in one ligand (intraligand exchange, ν_{intra}). In the limiting case of rapid exchange when the exchange frequency is considerably high than the characteristic time of ESR ($\nu_{ex} \gg \gamma_e\Delta a$), the spectra corresponding to these two types of exchange basically differ from each other. In the case of only intraligand exchange (the first type) the HFI of unpaired electron with "equivalent" ring protons of one ligand will be realized, the constant being equal to the half-sum of constants in the absence of exchange. In the case of solely interligand exchange (the second type) pair-wise equal HFI with para and meta-protons of two ligands (4- and 5- positions respectively) will be observed,

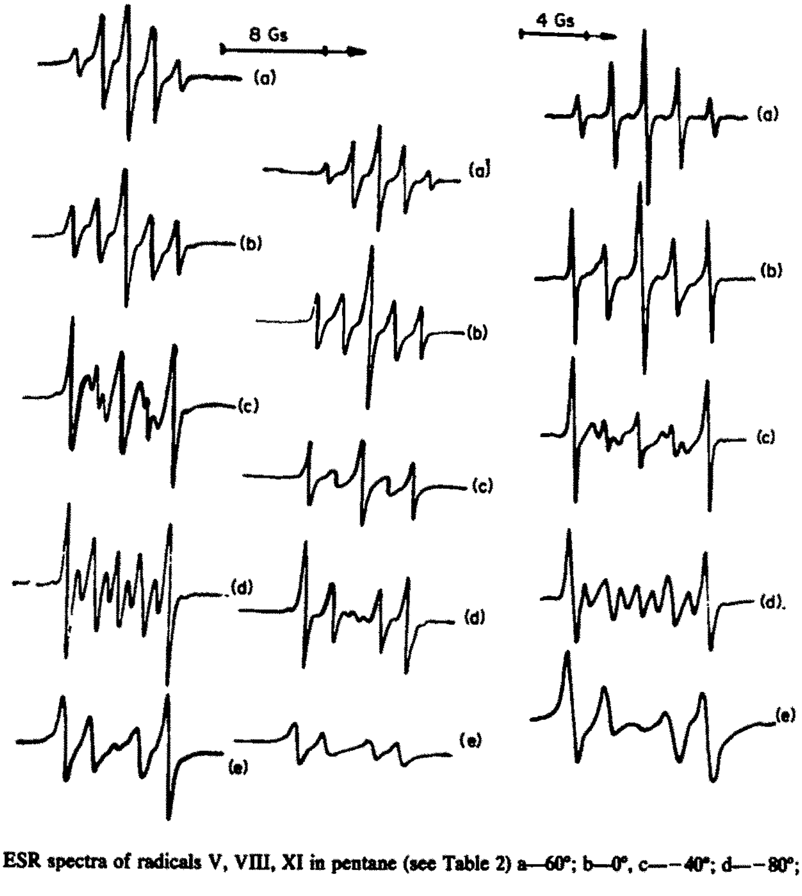


Fig. 2. ESR spectra of radicals V, VIII, XI in pentane (see Table 2) a—60°; b—0°, c—−40°; d—−80°; e—−100°.

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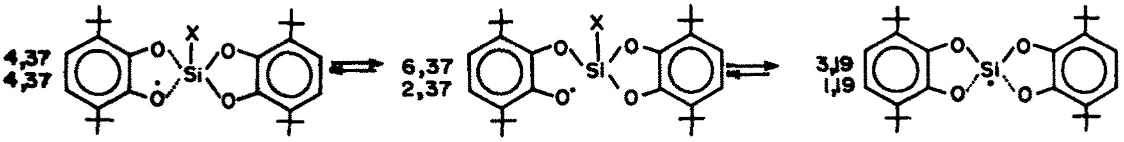
†HFI with ^{19}F(a_F5Oe) is observed for (XII) containing F.

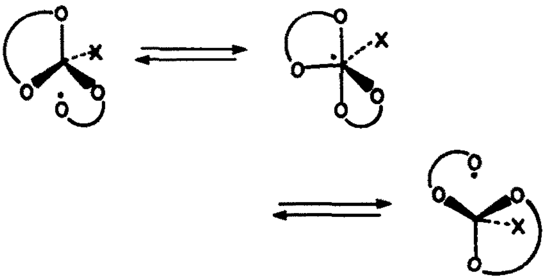
the constants being equal to half the constants in the spectrum of slow exchange. These spectral differences between intra and interligand exchange are illustrated below.



Experimentally observed spectral patterns do not correspond to the extreme cases, therefore realization of both type of exchange may be assumed in the radicals under study. In order to verify this assumption we calculated the contributions into the linewidths of the quintet (ΔT_2^{-1}) in the two cases considered[10] using the HFI constants for the limiting structures. The contribution of the central component is equal for both types of exchange, whereas for lines $M_I = \pm 1$ *it is different.* Four units of the central components make minimal contributions to the width (16 Oe^2) as compared with lines $M_I = \pm(35\ \text{Oe}^2)$ for the first type of exchange. This explains the unequal broadening of components at the initial stage of exchange retardation. Sharp weakening of the central component on further reduction of temperature may be due to predominance of the second type of exchange ($\nu_{inter} \gg \nu_{intra}$). Indeed, the minimal contribution into the width is made by lines with $M_I = \pm 1$ (9.6 Oe^2) as compared with the central component (16 Oe^2). The predominance of interligand exchange at low temperatures is indicated by the appearance of a nine-line spectrum, which may be assigned to intermediate appearance of triplet–triplets with HFI constants indicated above. The difference in line intensities is caused by fulfillment of the condition of intermediate exchange ($\nu_{ex} \sim \gamma_e \Delta a$) however, even quantitative considerations show the correctness of the assumption. Lines with $M_I = \pm 1, \pm 1$ do not broaden during exchange and lines with $M_I = \pm 1, 0$ and $M_I = \pm 1, \mp 1$ make minimal contributions to the linewidth (Table 3). It is these lines which during formation of the nine lines remain the most narrow.

These spectral features are typical of ESR spectra of all radicals with "pentacoordinated" silicon (V-XVIII, Table 2) in which the HFI constants are practically independent of substituent X. Differences are observed only in the exchange frequencies and, consequently, effects of broadening and transfromation of the multiplet into doublet of doublets is observed in a certain temperature range for each radical.

It should be noted when considering the mechanism of exchange of unpaired electron and bond in radicals (V-XVIII) that the presence of vacant d-orbitals at the Si atom apparently plays an important role in realization of tautomeric processes. It may be considered that at low temperatures, when the exchange is "frozen", the Si atom has tetrahedral configuration, the univalent O atom being coordinated to the Si atom. In the process of radical substitution at Si characterizing exchange under consideration the latter becomes truly pentacoordinated, acquiring the geometry of trigonal bipyramid (TBP) or tetragonal pyramid (TP).

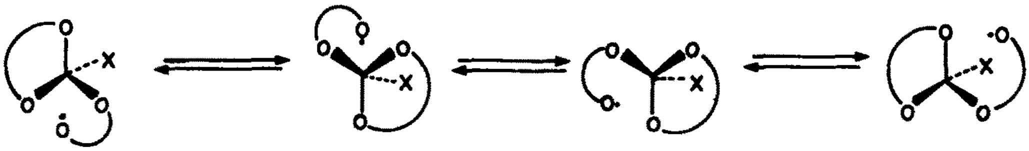


TBP apparently acts as a transition state and, in accordance with accepted notions,[18] the O atom in the apical position is substituted, while the principle of linear arrangement of the attacking univalent oxygen and the attacked SiO bond is retained. Assuming that the lifetime of the transition state is of the order of several vibrations, the processes of TBP pseudo-conversion resulting in apical and equatorial O atoms changing places may be considered unimportant. Such a mechanism of exchange should lead only to interligand exchange between oxygens in apical positions. Interligand exchange, as we have seen, is revealed specially at low temperatures and is caused by the coordination bond between univalent O and Si, which stabilizes the TBP-like structure. At higher temperatures this bond may rupture and rotation of the

Table 3. Contributions (ΔT_2^{-1}) into the width of multiplet components in ESR spectra of radicals V–XVIII on retardation of exchange between free valence and bond: type I exchange $\nu_{intra} > \nu_{inter}$, type II exchange $\nu_{intra} < \nu_{inter}$. Values of the contributions were obtained for HFI constants of ring protons $a^4 = 6.37$ Oe, $a^5 = 2.37$ Oe

Rapid exchange				Intermediate exchange			
				I type		II type	
M_I	Degeneration	$M_I = \sum_i M_i$	Degeneration	ΔT_2^{-1}	ΔT_2^{-1}(Oe^2)	ΔT_2^{-1}	ΔT_2^{-1}(Oe^2)
±2	1	±1, ±1	1	0			
±1	4	±1, 0	2	$\frac{1}{4}(a^4+a^5)^2+(a^4-a^5)^2$	35	$\frac{1}{4}(a^4-a^5)^2+(a^5)^2$	9.6
		0, ±1	2	$\frac{1}{4}(a^4+a^5)^2+(a^4-a^5)^2$	35	$\frac{1}{4}(a^4-a^5)^2+(a^4)^2$	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

free-radical ligand about the SiO bond may lead again to a similar structure, where another O atom of the ligand subjected to radical attack is aligned with the univalent O and Si atoms.



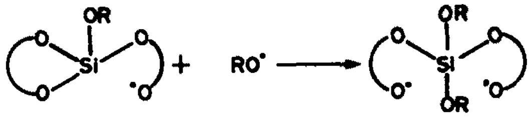
If the rotation frequency in sufficiently high all oxygens of the pyrocatechninic ligands will participate in exchange. Therefore the combination of interligand exchange with rotation of the free radical ligand is spectrally revealed as intraligand exchange. According to this model, viscosity of the solution should affect the rotation of the free radical ligand and consequently, the exchange rate. Indeed, the exchange rate for radicals (V, XV, XVII) is reduced by more than an order of magnitude when passing from solutions in pentane solutions to pure vaseline oil while the energy barrier increases by 2 kcal/mole. Determination of kinetic parameters in vaseline oil was carried out at 0–60° when ν_{intra} and ν_{inter} are comparable. We were unable to carry out spectral analysis at lower temperatures on account of sharp genral broadening of lines caused by increase of viscosity.

The proposed mechanism of exchange makes it possible to explain the observed differences in exchange frequences in radicals (V-XVIII). As mentioned above, spectral parameters are independent of the nature of substituent X at the Si atom and therefore do not influence noticeably the spin density distribution in these radicals. The observed changes in kinetical parameters of exchange presumably are connected with dimensions the attached X (see Table 2). With increase of the size of X the exchange frequency drops, according to the proposed mechanism this is explained by distortions of transition state geometry and distortion of the linear arrangement of exchanging O atoms.

Therefore, the obtained experimental data illustrate the classical model of radical substitution at tetrahedral Si atoms, which reflects the interligand character of exchange of free valency and bond. Rotation of free-radical moiety about the SiO bond with simultaneous interligand exchange leads to spectral manifestation of intraligand exchange.

3. *Biradicals with hexa-coordinated silicon*

Radicals discussed in the previous section were obtained by cleavage of the SiO bond in SP using appropriate reagents. It was found that radicals with pentacoordinated Si, formed during interaction of SP with an excess of radical reagents, interact with the excess of free radicals yielding biradicals.[22]



SP also easily reacts with various orthoquinones forming biradicals with three pyrocatechninic ligands[24] (Table 4).

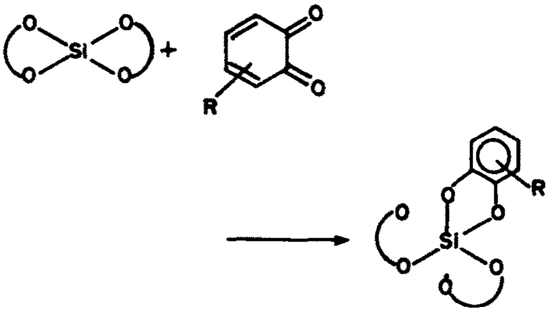
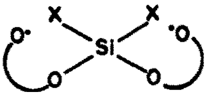


Table 4. Spectral parameters of biradicals XIX–XXVII



 is 3,6-di-t-butylpyrocatechinic ligands

N	X, X ligands	D(Oe ± 5Oe)	E(Oe ± 5Oe)
XIX	$(CH_3)_3CO$	340	20
XX	2,4,6-tri-t-butylphenoxyls	343	22
XXI	2,6-di-t-butyl-4-phenylphenoxyls	337	21
XXII	halvinoxyls	343	22
XXIII	2,2,6,6-tetramethyl-4-oxypiperidine-1-hydroxyls	332	22
XXIV	3,6-di-t-butylpyrocatechinic	325 (340)†	21 (0)†
XXV	3,5-ditert-butylpyrocatechinic	310 (290)	14 (14)
XXVI	3,5-di-t-butyl-6-chloro-pyrocatechinic	325 (325)	19 (19)
XXVII	tetrachloropyrocatechinic	325 (320)	25 (23)

†Parameters of spin–spin interaction obtained in solid polystyrene at 100° are given in parentheses.

EPRspectra of frozen solutions of these species are typical of biradical systems (Fig. 3) with effective spin–spin interaction of two unpaired electrons[11] revealed by the presence of splitting constants at zero field (D and E). Increase of temperature results in averaging of spin–spin interaction, and in liquid phase a single wide line, which narrows at higher temperatures, is observed (Fig. 3). The linewidth between points of maximal inclination at 25° is 25 Oe. Such variation is characteristic of stable radicals of the phenoxyl type[13] and confirms the structure of the species. In "semi-field" ($g = 4$) intensive absorption in frozen solutions is observed corresponding to transition $\Delta m = 2$ and is retained in toluene solutions up to $-80°$. Analysis of the spectra of the biradicals made it possible to determine parameters D and E (Table 4). The non-zero value of E points to the absence of axial symmetry in distribution of unpaired electrons in biradicals (XIX–XXVII). The value D characterizes the average distance between spins (r), which is determined by expression $D = g\beta(r)^{-3}$ in the point dipole approximation.[11]

D strongly depends on r, consequently, it may be assumed that the main contribution to D is made by spin density on the O atoms with unpaired electrons. Estimations of the spin density distribution in 3,6-di-t-butyl-2-oxyphenoxyl,[25] the structure of which is similar to that of radical ligands of the biradicals, indicate that the density on univalent O atoms is 0.3, then $r \sim 3$ Å. If biradicals XIX–XXVII (Table 4) have quasi-octahedral configuration due to coordination of unpaired electrons on vacant orbitals of Si atom, the univalent O atoms may be arranged in *cis* and *trans* positions in relation to each other. *trans* Positions for normal SiO bonds are separated by a distance of 3.3 Å. In the case of coordinated bonds these distances are presumably longer and it may be considered that $r \sim 3$ Å in the biradicals corresponds to the *cis* position of univalent O atoms. This is supported by the absence of axial symmetry ($E \neq 0$) in spectra of frozen solutions.

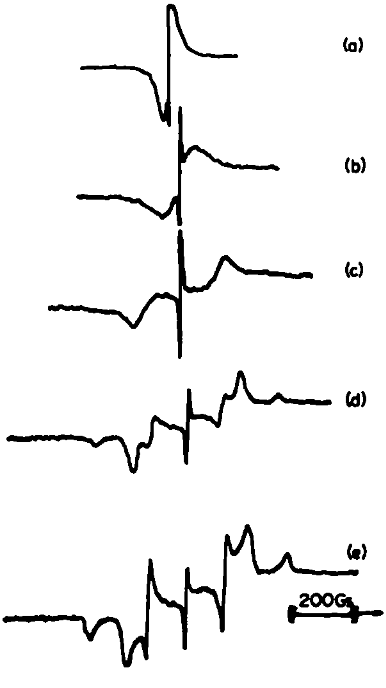


Fig. 3. ESR spectrum of biradical (XXIV) in toluene: a—20°; b—−40°; c—−80°; d—−100°; e—−140°.

On increase of temperature D decreases and E tends to zero. Such variation in the spectra of biradical systems is usually associated with the appearance of rotational mobility in the liquid phase and averaging of zero splitting constants (D and E). E determines the deviation of spin density distribution from axial symmetry. With increases of this deviation E increases as the difference between triplet levels in X and Y directions, axis Z is aligned with the external field. In systems with axial symmetry and in the case of rotation of asymmetrical systems in liquids this difference is averaged to zero.

Hence, the non-zero values of E in ESR spectra of frozen solutions of biradicals XIX–XXVII is connected with the asymmetric structure of these species and the absence of rotation in liquid phase. Provided that no processes occur in the biradicals on increase of temperature (unpaired electrons are localized in certain positions), the averaging of D and E should reflect only kinetical mobility. Since the dimensions and molecular weights of XIX–XXVII are comparable, the averaging should be of the same character. However, averaging of spin–spin interactions occurs differently. The spectra of XXIV and XXV in toluene at −80 point of axial symmetry ($E = 0$), whereas for XXVI and XVII $E \neq 0$.

The differences in averaging of D and E is especially distinct in the spectra of XXIV–XXVII in solid polystyrene (Fig. 4), where rotational mobility is absent. At low temperatures the spectra of all species are similar (Table 4), however at 100° only biradical XXIV with symmetrical and identical ligands does not exhibit splitting of triplet levels due to $E \neq 0$ (Fig. 4).

Note, that D practically does not vary in the temperature range (−120 ÷ 100°) and, consequently, the distance between unpaired electrons is constant. In biradicals XXV–XXVII E increases with the acceptor properties of the inequivalent ligand and reflects the effect of this ligand on the character of spin density distribution.

In our opinion the results obtained allow to assume that the difference in averaging of dipole–dipole interactions in biradicals XXIV–XXVII is due to intramolecular dynamic effects in these species, namely exchange of unpaired electron and bond. In XXIV this exchange involves to the same degree three identical

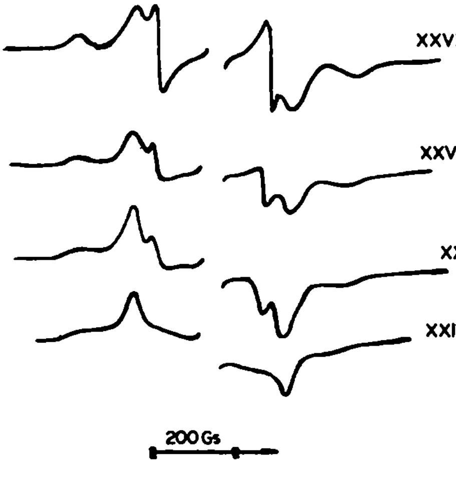


Fig. 4. ESR spectra of radicals XXIV–XXVII in solid polystyrene at 100°.

ligands and at high temperatures the silicon atom coordination number equal to 6 in the ESR time scale.

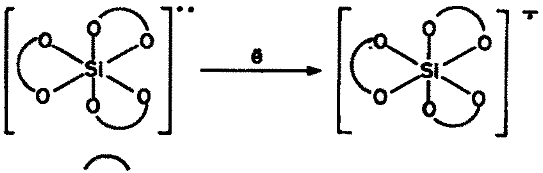
It should be noted that the line shapes in the spectrum of XXIV recorded in polysterene at 100° do not completely conform to a spectrum with ideal axial symmetry.[11] This suggests incomplete averaging of E in our experiments. In order to obtain an axially symmetrical spectrum the condition of rapid exchange should be fulfilled, i.e. $\nu_{ex} \gg \gamma_e \Delta a$, where Δa is the distance between exchanging lines equal to 3E in our case. Frequencies higher than $10^9 \, sec^{-1}$ satisfy this condition. Assuming that ν_{ex} in biradicals is close to ν_{ex} in free anion-radical (XXVIII) (see below), the intermediate case is realized, which is characterized by considerable broadening of lines and, consequently, change of their shape.

Variations in spectra of XXV–XXVII may be explained from this point of view. Introduction of inequivalent ligands removes degeneration of levels in the species, which are "multi-hole" systems. Removal of degeneration shaprly reduces the frequency of interligand exchange, resulting in incomplete triplet level splitting due to $E \neq 0$. This is clearly seen in the spectra of XXVI and XXVII containing chloro-substituted ligands: lines responsible for $E \neq 0$ are hardly broadened in the ESR spectra of these biradicals.

Hence, data discussed in this section point to the existence of interligand exchange in biradicals. Especially should be noted the existence of exchange processes in solid matrix (polystyrene). This fact indicates the decisive role played by coordination of univalent O atoms on vacant silicon orbitals in realization of exchange, which, as in the instances described previously, is intramolecular radical substitution. The fact that D remains constant in the entire temperature range studied and therefore the distance between unpaired electrons in polysterene matrixes, is evidence in favour of synchronous motion of unpaired electrons from ligand to ligand without variation of the distance between them.

4. *Anion-radicals with hexacoordinated silicon* ("six-hole" systems)

The main proof of the existence of biradicals is recording of the spectrum of anion-radical (XXVIII), during electrochemical reduction of biradical (XXIV):[24]



where  is the 3,6-di-t-butylpyricatechinic ligand.

Anion-radical (XXVIII) may be obtained by interaction of SP with alkaline salts of 3,6-di-t-butylorthosemiquinone.[26]

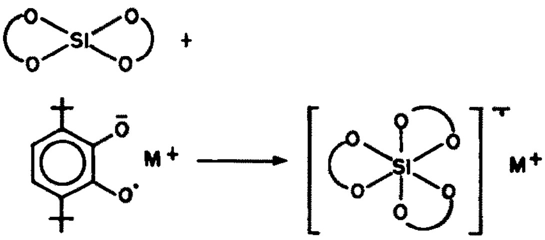


Figure 5 shows the spectra of XXVIII obtained during electrochemical reduction of XXIV. At low temperatures the triplet corresponds to interaction of unpaired electron with two equivalent protons of the same ligand ($a_H = 3.75$ Oe). Additional wide lines appear at higher temperatures. On further increase of temperature these lines narrow and the spectrum is converted into a septet (Fig. 5) ($a_H = 1.25$ Oe) due to the six "equivalent" protons of three ligands. These changes are fully reversible on temperature variation and indicate intramolecular exchange of unpaired electron and charge in XXVIII.

The electronic structure of XXVIII differs from the structure of usual anion-radicals obtained by reduction of neutral organic compounds in which the spin and charge densities are inseparable. In XXVIII the charge and spin density are localized in different ligands and redistribution of charge density proceeds independently of the exchange of free valence and bond.

The character of exchange in XXVIII is strongly dependent on the nature of the cation and solvent. As can be seen from Table 5, in weakly solvating media (contact ion pairs) the exchange frequency is by two or three orders of magnitude less (the activation energy higher) than in strongly solvating solvents (additions of hexamethapole) or in the presence of crown ethers which are strong solvating agents in relation to alkaline cations. In tetrahydrofuran and dimethoxyethane the Arrhenius temperature dependence of frequency is non-linear (Fig. 6), pointing to competition of two processes: solvation of cations with solvent molecules which causes attraction to free ions and acceleration of exchange (low temperatures) and increase of the fraction of contact ion pairs in which the exchange frequency is less than in solvated complexes with temperature. This competition

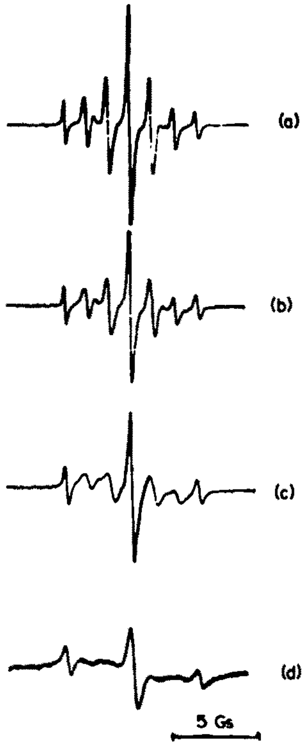


Fig. 5. ESR spectra of radical XXVIII, THF and tetrabutylammonium cation: a—−20°; b—−40°; c—−60°; d—−80°.

Table 5. Kinetic parameters of interligand exchange in ion pairs of anion-radical XXVIII

Cation†	Solvent	$\nu_{ex}(20°)s^{-1}$	$\nu_0 \times 10^{-11}$ (s^{-1})	$E_{act} \pm 0.5$ (kcal/mole)
TBA	THF	10^9	10	4.1
Na	THF + crown ether‡	4×10^8	10	4.6
Na	THF	2.5×10^6	7.4	7.4
Na	DME	2.2×10^6	22	8.1
K	THF	1.8×10^6	1.5	6.6
K	DME	1.2×10^6	7	7.9
Li	THF	6×10^5	3×10^{-4}	2.3
Li	DME	1.1×10^6	0.12	5.5

†TBA is the tetrabutylammonium cation.
‡Crown ether in 10^{-2} mole/l.

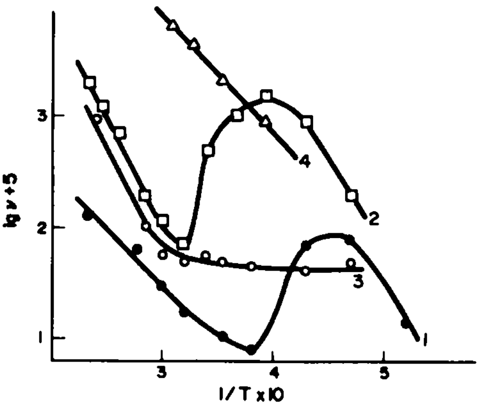
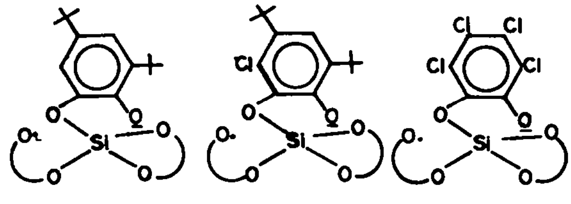


Fig. 6. Exchange frequency (ν_{ex}) vs 1/T for anion radical XXVIII in dimethoxyethane: 1—Li^+; 2—Na^+; 3—K^+; 4—TBA^+.

explains the observed dependence: exchange frequency drops with temperature increase (desolvation of cations), whereas at very high temperatures it again increases with a rather high effective activation energy.

Therefore it may be assumed that in contact ion pairs the exchange is determined by thermal motion of the cation from ligand to ligand, while in free ions by intramolecular radical substitution.

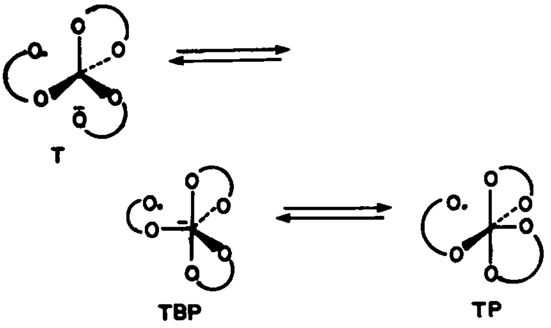
If one of the 3,6-di-t-butyl-pyrocatechinic ligands in XXVIII is replaced by a different ligand, the structure of this ligand will determine the character of exchange in the corresponding anion-radical. Such anion-radicals were prepared by interacting alkaline salts of 3,5-di-t-butylorthosemiquinone, 3,5-di-t-butyl-2-chloro-orthosemiquinone and orthochloranil (anion-radicals XXIX, XXX, XXXI).



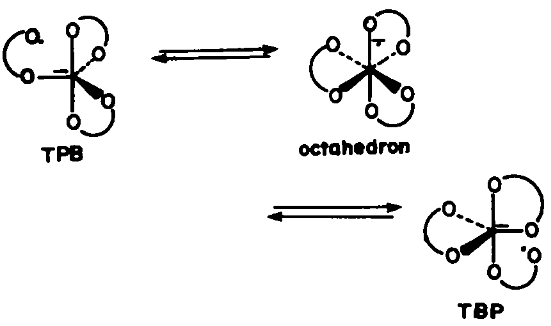
A common feature of XXIX–XXXI is that exchange of unpaired electron and bond involves only 3,6-di-t-butylpyracatechinic ligands, whereas the charge is localized on O atoms of the introduced ligands.[27] This unequivocally follows from ESR spectra of these species.

If the introduced ligand is symmetrical (XXXI) the unpaired electron "runs over" all O atoms of 3,6-di-t-butylpyrocatechinic ligands (equal HFI with four ring protons is observed in the entire temperature range). When the introduced ligand is not symmetrical (XXIX, XXX) pair-wise equivalent ring protons are observed in the spectra. The latter points to predominance of interligand exchange. It should be noted that these features are displayed in strongly solvating solvents such as THF-hexamethapole.[27]

Apparently, a donor–acceptor bond is formed between the O atom carrying a negative charge and the Si atom with the oxygen electron pair occupying the vacant d-orbital of the Si atom. This is enhanced by the solvating medium, which transfers the cation to the outer sphere. The tetrahedral structure of XXVIII–XXXI (T) in this case is converted into trigonal-bipyramid(TBP) or tetragonalpyramid(TP). Such structures are characterized by inequivalence of apical and equatorial bonds and by exchange between apical and equatorial positions as a result of pseudo-rotation.[28,29]

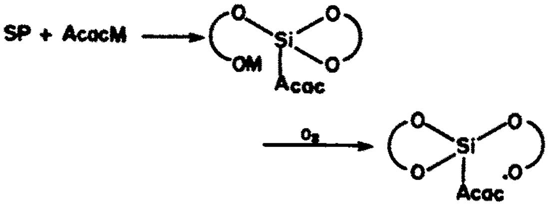


Thus, exchange in anion-radicals XXIII–XXXI may be considered as radical attack on the trigonal-bipyramid Si atom with formation of octahedral transition state.



At high rates of pseudo-rotation, typical of symmetrical structures (XXVIII) and which may occur both with and without exchange of unpaired electron and bond each TBP and TP position may be occupied by any O atom of the ligand and, although the elementary act of synchronous radical substitution proceeds through a linear transition state, the unpaired electron may be found on any O atom. These reasons explain the kinetic equivalence of intra- and interligand exchange. In the case of one inequivalent and non-symmetrical ligand (XXIX, XXX) the pseudo conversion frequencies may be lower than exchange frequencies, the latter being purely interligand in this case on account of the linearity of the transition state.

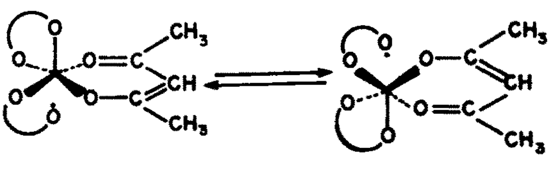
An interesting effect of stereochemical features on the character of exchange is observed in radical (XXXII) which contains an acetylacetonate ligand along with the 3,6-di-t-butylpyrocatechinic ligand. This radical is formed in the reaction of SP with acetylacetone (AcacH) or its salts according to scheme



where M-H, Co, Mn, Zn, Cd.

At temperatures above 20° (Fig. 7a) each component of the triplet ($a_H^4 = 2.4$ Oe) corresponding to ring protons in position are splitted into a triplet on account of the two protons in position 5 ($a_H^5 = 1.65$ Oe). The pair-wise equivalence of protons in positions 4 and 5 unambiguously indicates inter-ligand exchange in XXXII. At lower temperatures some components broaden (Fig. 7b) and at −100° the ESR spectrum displays a doublet of doublets ($a_H^4 = 4.8$ Oe, $a_H^5 = 3.3$ Oe) which corresponds to localization of free valency on one of the O atoms.

The coordination capacity of silicon in β-diketonate complexes greatly depends on its structure. β-Diketonate ligands form chelate bonds mainly in cationic complexes (siliconium salts).[30–32] In the presence of two or three organic substitutents at the Si atom the β-diketonate ligands do not display distinct bidentate properties.[33,34] Therefore, it may be assumed that the nature of the bond between acetylacetonate ligand and Si atom in XXXII will be intermediary between chelate and ordinary bonds with partial coordination of the CO group on the d-orbital of Si. Then, a TBP or TP geometry with low symmetry on account of the difference in attached ligands and in the character of SiO bonds with the acetylacetonate ligand may be assigned to radical XXXII. The pseudo-conversion frequencies in low-symmetry TBP or TP are usually small[35] and the observed interligand exchange proceeds only on account of the linearity of the transition state in the substitution reaction.[18]



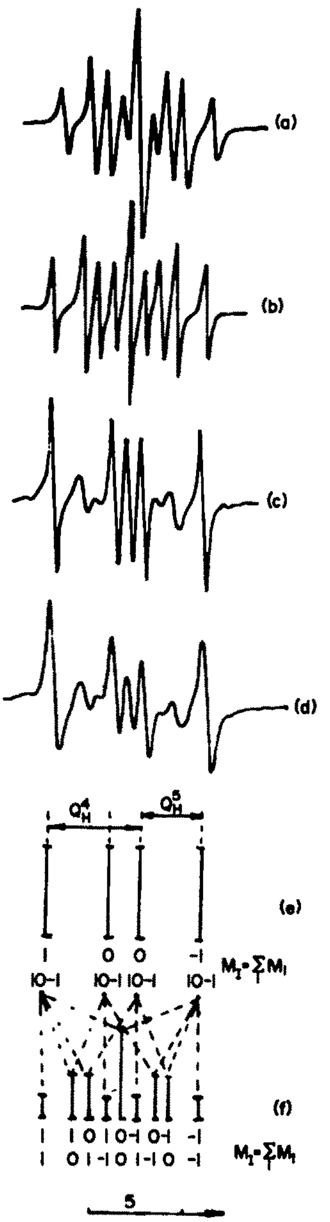


Fig. 7. ESR spectra of radical XXXII in pentane: a—60°; b—−40°; c—−60°; d—−100°.

Increase of viscosity does not noticeably retard exchange (vaseline oil). This apparently is connected with the tight arrangement of ligands around the central atom that hinders rotation of the free-radical moiety about the SiO bond, deminishing the effect of viscosity on the exchange process. This observation is in favour of coordination of the acetylacetonate CO to Si, since otherwise XXXII should be assigned to radicals of the type V–XVIII, the exchange in which depends on viscosity.

The viscosity of medium presumably does not affect the exchange frequency in anion-radicals XXVIII–XXXI because in weakly solvating solvents (THF, DME) at temperatures close to the m.p of these solvents the exchange frequency increases due to effective solvation of the cation (see above). For "hexacoordinated" radicals (biradicals, anion-radicals) the effects of intramolecular coordination of unpaired electrons and the close arrangement of the ligands to the central atom renders intramolecular exchange "insensitive" to viscosity of the solvent. Recall, that exchange in biradicals is observed in solid polystyrene matrixes (Section 3).

The examples of tautomerism in free Si-containing radicals described above, illustrate the decisive role of coordination of univalent oxygen on vacant Si orbitals in realization of tautomeric transitions, while the exchange, which is actually intramolecular radical substitution at Si, is determined by stereochemical features of the radicals. It is important that in radicals with penta- and hexacoordinated Si the principle of linearity of transition state of exchange reactions is retained and appearance of unpaired electron on any O atom of exchanging ligands is a result of either rotation of the free-radical ligand or the effect of pseudo-rotation of the initial structures.

Exchange of the unpaired electron and bond may be considered as a new type of delocalization of unpaired electron—delocalization with bond rupture.

REFERENCES

[1] H. Aurich and R. Stork, *Tetrahedron Letters* 555 (1972).

[2] A. I. Prokof'ev, N. N. Bubnov, S. P. Solodovnikov and M. I. Kabachnik, *Ibid.* 2479 (1973).

[3] A. I. Prokof'ev, N. A. Malysheva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov and M. I. Kabachnik, *Dokl. AN SSSR* **229**, 1128 (1976).

[4] S. G. Kukes, A. I. Prokof'ev, N. N. Bubnov, S. P. Solodovnikov, E. D. Korniets, D. N. Kravtsov and M. I. Kabachnik, *Ibid.* **229**, 877 (1976).

[5] A. I. Prokof'ev, N. A. Malysheva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, N. L. Komissarova, V. V. Ershov and M. I. Kabachnik, *Ibid.* **229**, 1398 (1976).

[6] A. I. Prokof'ev, A. A. Khodak, N. A. Malysheva, P. V. Petrovsky, N. N. Bubnov, S. P. Solodovnikov and M. I. Kabachnik, *Ibid.* **240**, 92 (1978).

[7] A. I. Prokof'ev, A. A. Khodak, N. A. Malysheva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov and M. I. Kabachnik, *Ibid.* **240**, 358 (1978).

[8] A. I. Prokof'ev, T. I. Prokof'eva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov and M. I. Kabachnik, *Ibid.* **234**, 845 (1977).

[9] A. I. Prokof'ev, N. A. Malysheva, N. N. Bubnov, S. P. Solodovnikov and M. I. Kabachnik, *Izv. AN SSR, Ser. Khim.* N9 1969 (1978).

[10] G. K. Fraenkel, *J. Phys. Chem.* 71, 139 (1967).

[11] J. E. Wertz and J. R. Bolton, *Electron Spin Resonance*. McGraw-Hill, New York (1972).

[12] A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance*. New York, Evanston, London (1967).

[13] A. L. Buchachenko and A. M. Wasserman, *Stabilnye radikaly* (Stable Radicals). Nauka, Moscow (1973).

[14] M. Szwarz, *Ions and ion pairs*. New York (1972).

[15] 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. AN SSSR* **239**, 1367 (1978).

[16] V. D. Pokhodenko, *Fenoksil'nye radikaly* (Phenoxyl Radicals), Naukova Dumka, Kiev (1969).

[17] N. A. Malysheva, A. I. Prokof'ev, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov and M. I. Kabachnik, *Izv. AN SSSR Ser. Khim.* 1186 (1977).

[18] K. U. Ingold, B. P. Roberts, *Free-radical Substitution Reactions*. Wiley-Interscience, New York (1971).

[19] A. I. Prokof'ev, S. P. Solodovnikov, I. S. Belostotskaya and V. V. Ershov, *Izv. AN SSSR, Ser. Khim.* 199 (1974).

[20] A. I. Prokof'ev, A. S. Masalimov, N. N. Bubnov, S. P. Solodovnikov and M. I. Kabachnik, *Izv. AN SSR, Ser. Khim.* 193 (1976).

[21] M. G. Voronkov, V. P. Mileshkevich and Yu. A. Yuzhelevsky, *Siloksanovaya svyaz* (Siloxane bond). Nauka, Novosibirsk (1976).

[22] 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. AN SSSR* **236**, 897 (1977).

[23] E. B. Zavelovich and A. I. Prokof'ev, *Chem. Phys. Letters* **29**, 212 (1974).

[24] 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. AN SSSR* **234**, 603 (1977).

[25] A. I. Prokof'ev, S. P. Solodovnikov, N. N. Bubnov and A. S. Masalimov, *Izv. AN SSSR, Ser. Khim.* 2488 (1976).

[26] A. I. Prokof'ev, T. I. Prokof'eva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov and M. I. Kabachnik, *Ibid.* N7, 1512 (1978).

[27] A. I. Prokof'ev, T. I. Prokof'eva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov and M. I. Kabachnik, *Ibid.* N9, 1961 (1978).

[28] R. S. Berry, *J. Chem. Phys.* 32, 933 (1960).

[29] P. Gillespie, F. Ramirez, I. Ugi and D. Marquarding, *Angew, Chem.* Inter. Edn. 12, 91 (1973).

[30] P. M. Pike and R. R. Luongo, *J. Am. Chem. Soc.* **87**, 1403 (1965); **88**, 2972 (1966).

[31] D. W. Thomson, *Inorg. Chem.* **8**, 2015 (1969).

[32] N. Serpone and K. A. Hersh, *J. Organometal. Chem.* **84**, 177 (1975).

[33] R. West, *J. Am. Chem. Soc.* **80**, 3246 (1958).

[34] T. J. Pinnavaie, W. T. Collins and J. J. Howe, *Ibid.* **92**, 4544 (1970).

[35] R. Luckenbuch, *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*. Stuttgart (1973).