MECHANISM OF THE INTRAMOLECULAR EXCHANGE OF THE UNPAIRED ELECTRON AND BOND IN FREE β-SUBSTITUTED PHENOXYL RADICALS OF THE ESTERS OF ORTHOSILICIC ACID

A. I. Prokof'ev, T. I. Prokof'eva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov, and M. I. Kabachnik

Studies on tautomerism in organosilicon free-radicals have led to the discovery of the so-called wandering valence, that is, intramolecular exchange of the unpaired electron and bond, in the following types of organosilicon acid esters:

In radical anions (RA) [1, 2]

In biradicals [2]

In radicals [3]

Here $\cdot$ designates the 3,6-di-tert-butylpyrocatechol ligand.

Although the Si atom is tetravalent in each of these structures, the pyrocatechol ligands become spectrally equivalent under exchange at rates higher than those corresponding to characteristic ESR times. The effective coordination number of the Si atom is therefore 6 in the first two of the above cases and 5 in the third.

The present work will present further instances of free radicals with "five" and "six"-coordinated silicon. The mechanism of exchange of free valencies and bonds in these radicals will be adduced from these and earlier data.

The fact that the siloxane bond readily cleaves under the action of various reagents [4] was drawn on to break one of the SiO bonds in silicon bis-3,6-di-tert-butylpyrocatechol (PC).

This procedure gives rise to the formation of a free radical, or to the formation of hydrolysis products (phenols) which oxidize to form free radicals.

The radicals with five-coordinated Si atoms were prepared by the interaction of PC with stable radicals [3].

\[
\begin{array}{c}
\text{PC} + \text{RO}^\cdot (\text{X}) \rightarrow \text{O}_5\text{Si}^\cdot \text{R}(\text{X}) \\
\end{array}
\]

The halogens interact with PC in the same manner (X = I, Br, Cl). It is clear that the X\textsuperscript{1} will be consumed in reacting with the solvent. The spectra of Fig. 1 were obtained after vacuum addition of an excess PC to pentane solutions of the halogens. The quintet appearing at temperatures in excess of 20\textdegree C (\(a_H = 2.2 \text{ Oe}\) results from interaction of the unpaired electron with the four "equivalent" protons of the two pyrocatechol ligands (Fig. 1a). Reduction of the temperature localizes the unpaired electron on one of the O atoms and carries the quintet to a doublet of doublets (\(a_{\text{H1}} = 6.37 \text{ Oe}, a_{\text{H2}} = 2.37 \text{ Oe}\)) (Fig. 1e). The fact that this change is reversible and proceeds through various intermediate stages of line broadening in the quintet is an indication of a gradual slowing of the exchange of the free valence and bond (Fig. 1b, c, d).

The radicals formed in the reaction of PC with molecular iodine are quite sensitive to light; subjected to UV irradiation in the resonator of the ESR spectrometer, their concentration falls off precipitately, only to rise again once the light has been turned off. The indication here is that radical dissociation into the original PC and iodine proceeds reversibly.

\[
\begin{array}{c}
\text{I}_2 + \text{PC} \rightarrow \text{PC} + \text{I}^\cdot \\
\end{array}
\]

The interaction of PC with HCl, HBr, and HI under similar conditions gives rise to similar ESR spectra which are similarly affected by changes in temperature. The reaction of PC with HF leads to the formation of a fluorine-containing radical whose ESR spectrum shows a doublet from the one \(1^{\text{H}}\text{F} (a_F = 5.0 \text{ Oe})\), each component of the doublet breaking down to a quintet (\(a_H = 2.2 \text{ Oe}\)) under the action of the four protons of the pyrocatechol ligands. Radical formation in these reactions can be represented through the following scheme:

\[
\begin{array}{c}
\text{PC} + \text{HX} \rightarrow \text{O}_5\text{Si}^\cdot \text{X} \rightarrow \text{O}_5\text{Si}^\cdot \text{H} \\
X = \text{I}, \text{Br}, \text{Cl, F, MeCOO.} \\
\end{array}
\]

Oxidation of the intermediate phenol by the oxygen of the atmosphere showed that 3,6-di-tert-butylpyrocatechol readily oxidizes in solution to form a semiquinone radical or even orthoquinone itself.

The siloxane bond in the PC also cleaves under the action of semiquinone radicals of various types (Table 1).

\[
\begin{array}{c}
\text{Q} + \text{QH}_2 \rightleftharpoons 2\text{QH} \\
\text{PC} + \text{QH} \rightarrow \text{O}_5\text{Si}^\cdot \text{Q} \\
\end{array}
\]

Here Q designates quinone, \(\text{QH}_2\) is the corresponding pyrocatechol or hydroquinone, and \(\text{QH}\) is the semiquinone radical [cf. Table 1, compounds (VI)-(IX)].

The ESR spectra indicate the formation of a series of radicals and biradicals in the reaction of PC with di-tert-butyl peroxide.

\[
\begin{array}{c}
\text{PC} + \text{Me}_3\text{CO}^\cdot \rightarrow \text{O}_5\text{Si}^\cdot \text{Me}_3\text{CO} \\
\end{array}
\]

The original monoradical quintet spectrum gradually disappears and is replaced by a single wide line, which is, in turn, transformed on freezing into the spectrum of a biradical of similar structure [1, 2] with parameters characteristic of zero splitting, \(D = 340 \text{ Oe}, E = 20 \text{ Oe}\). Half-field signals (\(g = 4\)) also appear in the spectra of the frozen solutions.

The exchange rate (\(\nu_{\text{ex}}\)) in radicals (I)-(XIV) was calculated from the broadening of the hyperfine structure lines, and the preexponential factor (\(\nu_0\)) and the exchange activation energy (\(E_a\)) obtained from the temperature variation of the rate (cf. Table 1). The data show that there is a tendency for \(\nu_{\text{ex}}\) to diminish, and