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ESR study of free-radical intramolecular transfer of a hydrogen atom: mechanisms and kinetics of the reactions

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A method for preparing $>Si(R_1)(R_2^{\cdot})$ structures ($R_1 = CH_3$, CD_3, or $CH_2{-}CH_3$, $R_2^{\cdot} = CH_2{-}CH_2^{\cdot}$ or $CD_2{-}CD_2^{\cdot}$) grafted to a silica surface is developed. The reactions of intramolecular transfer of H (D) atoms between the R_1 and $R_2^{\cdot}$ fragments were studied by ESR. The directions and kinetic parameters of these reactions were established.

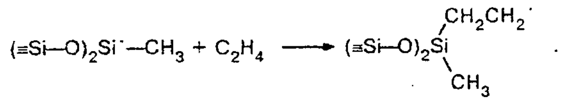
Key words: free radical, ESR, kinetics, surface.

Isomerization of alkyl radicals *via* intramolecular transfer of a hydrogen atom plays an important role in various chemical processes. However, there are relatively few reliable kinetic data concerning this type of reaction. Normally these data are obtained by analyzing complex chemical processes that include isomerization as one of their steps. In these cases, a number of assumptions are made that are not always reliably justified. For this reason, the data reported by various authors are often different.[1,2]

In this paper, we propose an original method for preparing structures of the type $(\equiv Si{-}O)_2Si(R_1)(R_2^{\cdot})$, where $(\equiv Si{-}O)_2Si<$ is a fragment of the silica surface, R_1 is CH_3, CD_3 or $CH_2{-}CH_3$ and $R_2^{\cdot}$ is $CH_2{-}CH_2^{\cdot}$ or $CD_2{-}CD_2^{\cdot}$. The method for preparing these structures is based on the chemical modification of silylene type centers stabilized on the surface of activated silica[3] (so-called "reactive silica" (RSi)). Two-coordinated silicon atoms efficiently accept $R_1^{\cdot}$ radicals ($CD_3^{\cdot}$, $CH_3^{\cdot}$, $C_2H_5^{\cdot}$) thus giving the corresponding paramagnetic complexes (see Ref. 4), for example:

$$(\equiv Si{-}O)_2Si{:} + CH_3^{\cdot} \longrightarrow (\equiv Si{-}O)_2Si^{\cdot}{-}CH_3.$$

Silicon-centered radicals add molecules of unsaturated hydrocarbons to yield carbon-centered radicals,[5] for example:

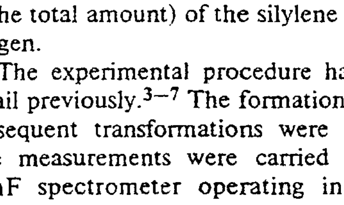


$$(\equiv Si{-}O)_2Si^{\cdot}{-}CH_3 + C_2H_4 \longrightarrow (\equiv Si{-}O)_2Si\begin{matrix}CH_2CH_2^{\cdot}\\ CH_3\end{matrix}.$$

Low-molecular-weight radicals $R_1^{\cdot}$ were generated using various types of surface defects. Two main types of structural defects are stabilized on the surface of activated silica: paramagnetic $(\equiv Si{-}O)_3Si^{\cdot}$ radicals, and diamagnetic $(\equiv Si{-}O)_2Si$ silylene groups.[3] When paramagnetic $(\equiv Si{-}O)_3Si^{\cdot}$ radicals are involved, the oxysilyl radicals, which are obtained by oxidation of $\equiv Si^{\cdot}$ radicals (see Ref. 6) act as active centers. In this case, the $R_1^{\cdot}$ radicals are formed according to the following scheme:

$$(\equiv Si{-}O)_3Si{-}O^{\cdot} + CH_4 \longrightarrow (\equiv Si{-}O)_3Si{-}OH + CH_3^{\cdot}.$$

The other method is based on the reaction of surface dioxasilirane groups (DOSG) with molecules of saturated hydrocarbons:[7]



DOSG are obtained[3] by oxidation of some (5—10% of the total amount) of the silylene centers by molecular oxygen.

The experimental procedure has been described in detail previously.[3—7] The formation of radicals and their subsequent transformations were monitored by ESR. The measurements were carried out on an EPR-20 IKhF spectrometer operating in the X-range. The radiospectroscopic characteristics of various types of paramagnetic centers are listed in Table 1. The substituent at the silicon atom has virtually no effect on the constants of HFC; therefore R is any of the hydrocarbon fragments encountered in the radicals that we studied. The magnitudes of the *g*-factors for the substituted alkyl

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Table 1. Radiospectroscopic characteristics of the radicals[a] (mT)

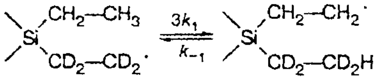
Type of radical	T/K	$a(\mathrm{H}_\alpha)$	$a(\mathrm{H}_\beta)$	a(D)
$>\mathrm{Si(R)(CH_2{-}CH_2^{\cdot})}$	295	2.17[b]	2.04	≤0.05
$>\mathrm{Si(R)(CH_2{-}CHD^{\cdot})}$	373	2.17[c]	2.04	0.36
$>\mathrm{Si(R)(CD_2{-}CD_2^{\cdot})}$	373			0.34
$>\mathrm{Si(R)(CD_2{-}CDH^{\cdot})}$	373	2.18		0.34
$>\mathrm{Si(R)(^{\cdot}CH{-}CH_3)}$[d]	295	$a_\parallel(\mathrm{H}_\alpha) = 2.8$ $a_\perp(\mathrm{H}_\alpha) = 1.85$	2.54	

[a] The error in determination of the constants was 0.02 mT. [b] For the $(\equiv\mathrm{Si{-}O})_3\mathrm{Si{-}CH_2{-}CH_2^{\cdot}}$ radical, $a(\mathrm{H}_\alpha) = 2.3$ mT, $a(\mathrm{H}_\beta) = 2.05$ mT (see Ref. 5). [c] The HFC constants at the hydrogen atoms for this radical were assumed to be identical to those for **2**$^{\cdot}$. [d] In the $(\equiv\mathrm{Si{-}O})_3\mathrm{Si{-}CH^{\cdot}{-}CH_3}$ radical, the corresponding constants are equal to[5] $a_\parallel(\mathrm{H}_\alpha) = 2.54$ mT, $a_\perp(\mathrm{H}_\alpha) = 1.73$ mT and $a(\mathrm{H}_\beta) = 2.45$ mT.

radicals under consideration lie in the 2.0026±0.0002 range.

Mechanisms of migration of H (D) atoms

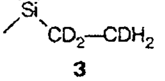
Figure 1, *a* shows the ESR spectrum of radical **1**. The observed hyperfine structure of the spectrum consists of nine components occuirring as a result of coupling of the unpaired electron with two α- and two β-deuterium nuclei (see Table 1); the difference between the HFC constants in this case is smaller than the width of an individual component. Keeping the sample at 246 K is accompanied by a decrease in the intensity of this signal and by the appearance of new lines in the spectrum. The latter are marked by asterisks in Fig. 1, *b*. These lines belong to radical **2** (reaction (1)) (the factor of 3 at k_1 is due to the presence of three protons in the methyl group).



1 **2** (1)

A similar ESR signal has been recorded previously[5] for the $\equiv\mathrm{Si{-}CH_2{-}CH_2^{\cdot}}$ radical. During the process illustrated by reaction (1), the overall concentration of paramagnetic centers (PMC) remains approximately constant. When the sample is kept at 246 K, the degree of conversion approaches 85%. This value corresponds to the state at which the rates of the forward and reverse reactions are equal (see equilibrium (1)).

When the sample is heated to 270 K, the ESR spectral pattern becomes more complex, because PMC incorporating both D and H atom appear in the system. In particular, we recorded the ESR spectrum of radical **3**.



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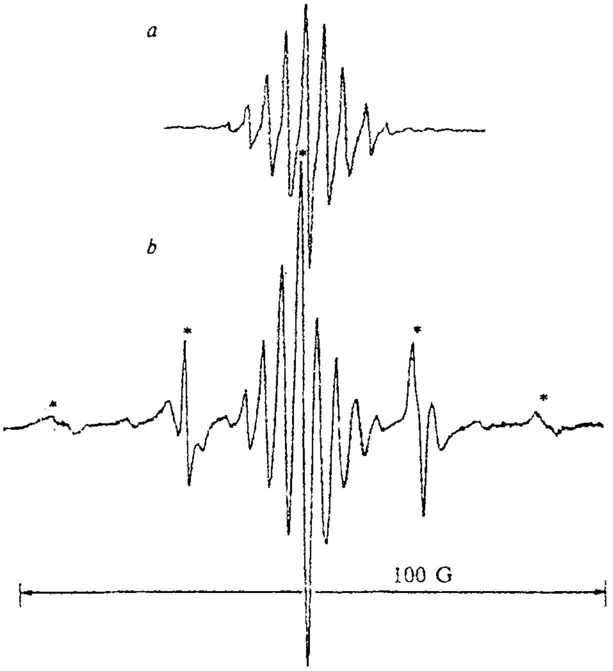
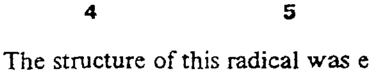


Fig. 1. ESR spectra of free radicals grafted to a silica surface (recorded at 230 K): radical **1** (*a*); sample kept for 20 min at 246 K (spectrum recorded at twice the amplification as that of *a*) (*b*).

As would be expected, the transfer of a D atom between the terminal groups occurs at a markedly lower rate (in a classic isotope effect, the ratio of the rate constants is expected to be 10—20).

In addition we detected 1,4-migration of an H atom in radical **4** (its ESR spectrum is shown in Fig. 2, *a*). When the sample is kept at 295 K for a long period, the concentration of radical **4** decreases, while the intensity of the ESR signal corresponding to new PMC increases in parallel. The ESR spectrum of the reaction product is shown in Fig. 2, *b*. It is associated with free radical **5** (reaction (2)).



4 **5** (2)

The structure of this radical was established based on the interpretation of its ESR spectrum. The hyperfine structure of the ESR spectrum of the radical formed is due to the coupling of the unpaired electron with three magnetically equivalent β-protons of the methylene group and one α-proton (see Table 1). The tensor of the hyperfine coupling of the unpaired electron with the α-proton is anisotropic. In radical **5**, the α-proton may change its position as a result of internal rotation around the Si—C bond; this can result only in partial averaging

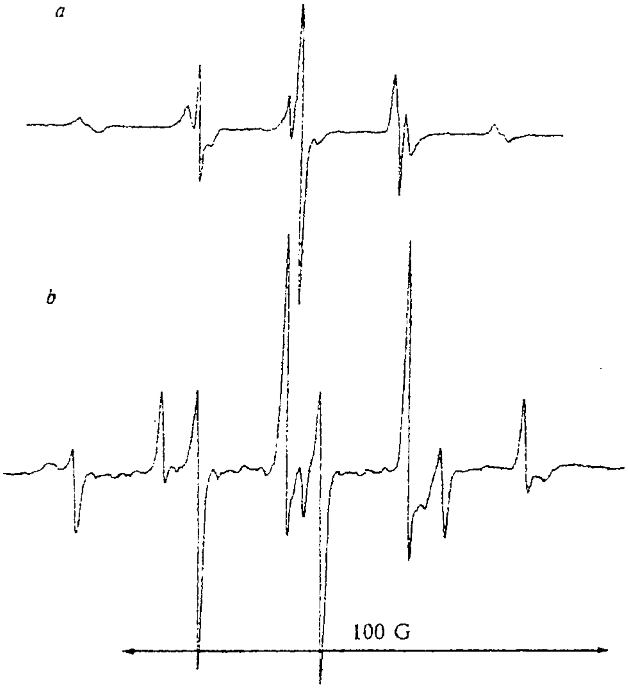


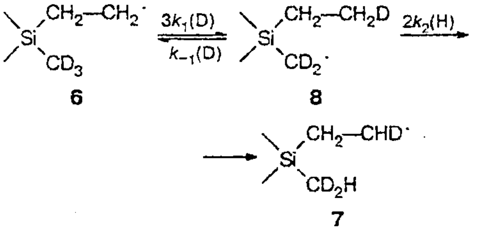
Fig. 2. ESR spectra of free radicals grafted to a silica surface recorded at 295 K: **4** (*a*) and 5 (*b*).

of the anisotropy of hyperfine coupling. At room temperature, this rotation is virtually free.

Thus, the presented experimental data imply that the transfer of H and D atoms between the terminal groups in the hydrocarbon fragments is the process that occurs at the highest rate in radicals **1** and **4**. We were able to detect this process owing to the use of the isotopic label (the ESR spectra of the protonated forms of both radicals are identical). The 1,4-migration of the H atom occurs at a lower rate.

The 1,4-migration of hydrogen was also studied in relation to systems containing a methyl group as the R_1 fragment.

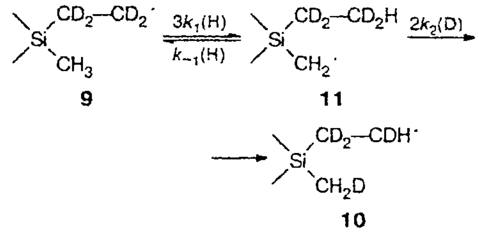
At 373 K (*i.e.*, at a temperature markedly higher than that in the case of systems **1** and **4**), fragment **6** is converted into 7. This reaction can occur only *via* the intermediate formation of radical **8** (reaction (3)).



(3)

However, we did not detect the ESR spectrum of radical **8** in our experiments. With allowance for the accuracy of our measurements, this implies that the concentration of these radicals does not exceed 0.1—0.01 of the overall number of radicals in the system.

A similar situation is observed in the case of radical **9**. Storage of the sample at 373 K was accompanied by the transformation of **9** into **10** (reaction (4)). However, in this case, too, the intermediate **11** was not detected.



(4)

Thus, radicals **8** and **11** are substantially more active with respect to the abstraction of hydrogen atoms than the initial radicals **6** and **9**, and, hence, their steady-state concentrations are lower.

This conclusion is also supported by the fact that keeping the $>Si(CH_3)(CH_2—CH_2^{\cdot})$ radical at 373 K for 30 min is not accompanied by a variation of the ESR spectral patterns of paramagnetic centers.

Kinetic regularities of the processes

We also determined the kinetic characteristics of some of the processes discussed above. By measuring the ratio of the concentrations of PMC under conditions where the rates of the forward and reverse reactions are equal (or nearly equal), we have determined the equilibrium constants. The equilibrium constant for reaction (1) amounted to $K(1) = 5\pm0.5$. Since $K(1) = 3k_1/k_{-1}$, then $k_1/k_{-1} = 5/3$. The difference between the rate constants of the forward and reverse reactions may be due to both different pre-exponential factors and different energies of zero-point vibrations of these radicals, whose chemical natures are identical but whose isotope compositions are dissimilar.

For the **6** $\rightleftharpoons$ **8** and **9** $\rightleftharpoons$ **11** processes, we were able to estimate the equilibrium constants only roughly: $K \leq 0.1$.

The rate constants for the **1** $\longrightarrow$ **2**, **4** $\longrightarrow$ **5**, **6** $\longrightarrow$ **7**, and **9** $\longrightarrow$ **10** radical transformations were also measured (Table 2). In all the cases studied, the kinetics of transformations obeyed a first-order equation. For processes (1) and (2), the values obtained correspond to the rate constants of the elementary reactions. In the case of processes (3) and (4), which occur *via* intermediate species, we measured the effective rate constants. According to the approximation made using the method of quasi-steady-state concentrations for the intermediate radical (**8**), the following relation can be written for process (3): $k(3) = 3k_1(D)\cdot 2k_2(H)/[k_{-1}(D) + 2k_2(H)]$. Since $k_{-1}(D) << k_2(H)$, then $k(3) = 3k_1(D)$.

Table 2. Rate constants of free-radical processes of intramolecular transfer of an H (D) atom

Type of process	T/K (±1)	k/s^{-1}
(1)	246	$(6.6\pm0.7)\cdot10^{-4}$
(2)	295	$(1.2\pm0.1)\cdot10^{-4}$
(3)	373	$(5\pm0.5)\cdot10^{-5}$
(4)	373	$(2\pm0.2)\cdot10^{-4}$

Using the same approximations, the effective rate constant for the formation of radical **10** (reaction (4)) can be represented in the following form:

$$k(4) = 3k_1(\mathrm{H})\cdot 2k_2(\mathrm{D})/(k_{-1}(\mathrm{H}) + 2k_2(\mathrm{D})).$$

In this case, $k_2(\mathrm{D}) << k_{-1}(\mathrm{H})$. Assuming that $k(\mathrm{D}) = \alpha k(\mathrm{H})$ and that α does not depend on the type of reaction, $k(4)/k(3) = 2$. From the experimental results, it follows that $k(4)/k(3) = 4$ (see Table 2).

Thus, using an original procedure for preparing hydrocarbon groups grafted to the surface of a solid, the kinetics of free-radical intramolecular transfer of an H (or D) atom was studied for the first time by direct spectral methods. The 1,5- and 1,4-migrations of H (and D) atoms between hydrocarbon fragments of various structures were investigated. It was found that the thermoneutral 1,5-migration of a hydrogen atom in the systems considered occurs at a higher rate than the exothermal 1,4-migration. This result is related to the fact that the strain energy of a cyclic transition state increases as the number of atoms in it decreases (see, for example, Ref. 1).

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