Mechanisms of processes involving β-substituted cyclopropyl radicals. Ring expansion in the reaction with CO

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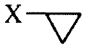
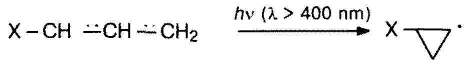
The reaction of β-substituted cyclopropyl radicals with CO was studied by ESR. The acyl radical resulting from the addition of CO to the cyclopropyl radical was detected. At temperatures near 270 K, an intramolecular rearrangement of the acyl radical affords substituted 2-oxocyclobutyl radicals (ring expansion reaction). Mechanisms for the free-radical transformations studied were suggested.

Key words: β-substituted cyclopropyl radicals, ESR; reactivity.

Previously[1] we developed methods for the preparation of β-substituted cyclopropyl radicals  grafted to the surface of a solid (SiO_2), where $X = \geqslant Si$, $\geqslant Si{-}O$, $\geqslant Si{-}CH_2$, $\geqslant Si{-}O{-}CH_2$ ($\geqslant Si$ is a silicon atom on the surface of a solid). This opened up possibilities for experimental studies of the mechanisms of processes involving these highly reactive intermediates. In this paper we present the results of a study of the reaction of β-substituted cyclopropyl radicals with CO molecules.

Allyl radicals are known[4] to undergo photocyclization under the action of light (λ = 410 nm). Similar results have been obtained for substituted allyl radicals grafted to the surface of highly dispersed silica (A-300 Aerosil):[1]



1 **2**

We used this method to prepare β-substituted cyclopropyl radicals

$X = (\geqslant Si{-}O{-})_3Si{-}O{-}CH_2$ (≡C),

$(\geqslant Si{-}O{-})_2(H{-}O{-})Si$ (≡Si).

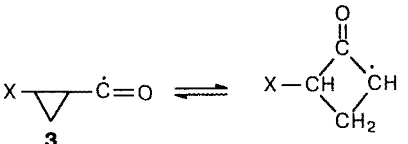
Free radicals were detected by ESR spectroscopy (X range).

Cyclopropyl radicals react with CO molecules already at 77 K giving acyl radicals in a quantitative yield:

2 **3** (1)

The doublet structure of the ESR spectrum of radical (**3**) (a_H = 0.85±0.5 mT) is due to the coupling of the unpaired electron with the β-proton of the cyclopropane ring (Fig. 1). The g_{iso} = (2.0005±0.0005) value is smaller than the *g*-factor of free electron (2.0023). The constants of the hyperfine coupling (HFC) of the unpaired electron with the ^{13}C nucleus are 12.9±0.1 (X = (≡Si)) and 12.7±0.1 mT (X = (≡C)), which is typical of acyl type radicals. For the formyl radical, $a_{^{13}C}$ = 13 mT and g_{iso} = 2.001 (see Ref. 5).

Radical (**3**) is thermally stable up to 260—270 K. At higher temperatures, the concentration of acyl radicals decreases, and a signal corresponding to a new radical species appears (see Fig. 1). This transformation is not accompanied by the formation of any gaseous products (for example, evolution of CO); it is an intramolecular rearrangement involving expansion of the cyclopropane ring:



3 **4** (2)

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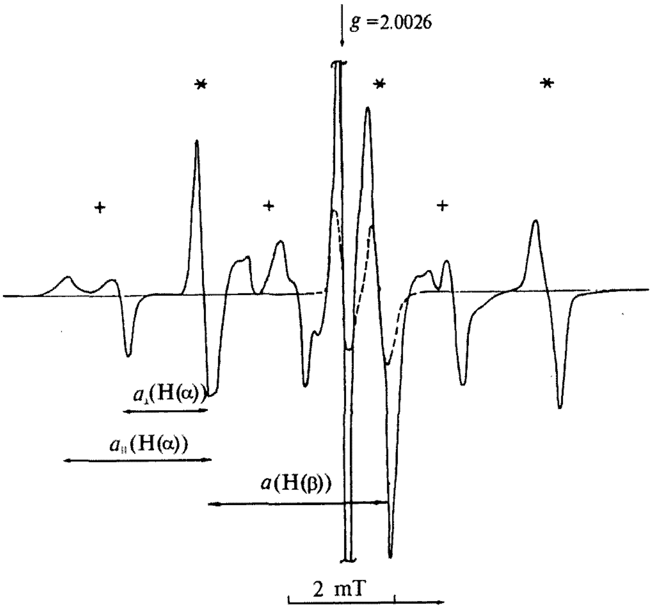


Fig. 1. ESR spectra of radicals **3** at 268 K (dashed line) and **4** with X = (≡Si), T = 298 K. The central part of the signal is disturbed by superposition of a narrow single line of an admixture center (g = 2.0026).

Reaction (2) is reversible; therefore, the ESR spectrum shown in Fig. 1 is a superposition of two signals. The equilibrium constant of this process (K_{eq}(298 K) = N(**3**)/N(**4**)) depends on the nature of the substituent X and amounts to 0.1 (X = (≡Si)) or 0.2 (X = (≡C)).

The ESR spectrum of the reaction product consists of six components, the ratio between their integral intensities being close to 1 : 1 : 2 : 2 : 1 : 1, *i.e.*, it is a doublet (1 : 1) of triplets (1 : 2 : 1). One of these triplets consists of slightly asymmetrical separate lines (see Fig. 1, asterisks), whereas the components of the other triplet (see Fig. 1, crosses) have clear-cut anisotropic shapes.

Radiospectroscopic parameters of the observed ESR spectrum are presented in Table 1. The anisotropic HFC tensor for the hydrocarbon radical should be attributed to the α-proton, while the other two tensors should be assigned to the two magnetically equivalent β-protons incorporated in the radical.[5]

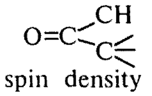
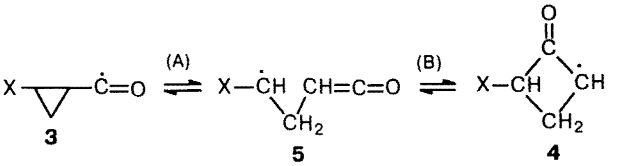
The isotropic value of the g-factor of the radical formed and the value of anisotropy are typical of the  $O{=}C{<}^{\dot{C}H}_{C{\leqslant}}$ free-radical moiety in which some of the spin density is localized on the oxygen atom of the carbonyl group.[6] The ESR spectrum of the product of reaction (2) (^{13}CO) exhibits an additional doublet splitting of each of the HFC components (see Table 1). The magnitude of the splitting is typical of the ^{13}C atom (I = 1/2) located in the α-position with respect to the unpaired electron.[5]

Table 1. Radiospectroscopic characteristics (mT) of radicals (**4**) (298 K)

X	(≡Si)	(≡C)
$g_{\parallel}$	2.0067±0.0005	—
$g_{\perp}$	2.0036±0.0005	
g_{iso}	2.0046±0.0005	2.0051±0.0005
$a_{\parallel}$(H(α))	2.68±0.05	—
$a_{\perp}$(H(α))	1.61±0.05	—
a_{iso}(H(α))	1.94±0.06	1.92±0.05
a_{iso}(H(β)-1)	3.30±0.05	3.45±0.15
a_{iso}(H(β)-2	3.30±0.05	3.45±0.15
a_{iso}(^{13}C)	1.43±0.05	1.43±0.05

Another characteristic feature of the radical formed is that its molecule contains two β-protons with large HFC constants, which almost do not change in the 77—300 K temperature range. This indicates that the barrier to the rotation around the C(α)—C(β) bond in the radical is high and makes it possible to speak of its rigid cyclic structure. Similar values of the constants of the HFC of the unpaired electron with β-protons have been obtained for the cyclobutyl radical.[7] A nearly planar structure of the substituted 2-oxocyclobutyl radical (which has also been confirmed by quantum-chemical calculations) accounts for the large constant of the HFC of the unpaired electron with β-protons and for its slight temperature dependence.

It may be assumed that the conversion of radicals (**3**) into (**4**) occurs *via* an intermediate linear species (**5**):

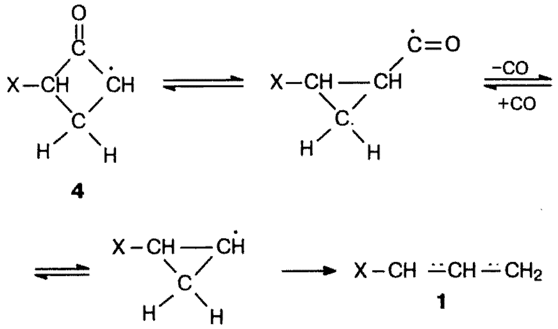


Its subsequent cyclization may follow two pathways (A and B); therefore, **5** is the common intermediate for the interconversion of **3** and **4**. According to at which particular carbon atom of the C=C bond the free-radical addition occurs, intermediate **5** yields radicals with different cyclic fragments.

We were not able to detect intermediate **5** by ESR, which points to it low thermodynamic stability, compared to radicals **3** and **4**.

At room temperature, further free-radical transformations occur in this system; their rate depends on the CO pressure and is maximum at $p_{CO} < 10^{-4}$ Pa. Under these conditions, the concentrations of radicals **3** and **4** synchronously decrease, CO is evolved, and the initial allyl radicals (whose photolysis gave cyclopropyl type radicals) are quantitatively regenerated. The overall amount of CO evolved in this reaction corresponds to its quantity absorbed in the formation of the acyl radicals by reaction (2).

Judging from the structures of radicals **3**, **4**, and **5**, one may assume that the CO molecules are liberated due to decomposition of acyl radicals **3**, and the allyl radicals result from the thermal decomposition of the cyclopropyl type radicals thus formed:[1,2]



As the CO pressure increases, the rate of reaction decreases. In an atmosphere of this gas, the reverse addition of CO to the cyclopropyl radicals prevents their decomposition yielding allyl radicals. Data on the kinetic features of the processes studied will be presented in the next communication.

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