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ESR study of radicals obtained from vinylalkoxysilanes and their adducts with branched fluoroalkenes

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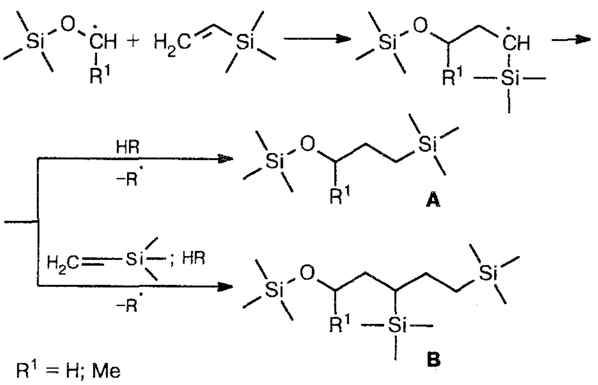
ESR spectra of radicals obtained by abstracting a hydrogen atom from methylvinyldimethoxysilane and methylvinyldiethoxysilane through the action of the *tert*-butoxy radical were studied. It was shown that the radicals appearing react with branched fluorinated olefins to give relatively stable radical adducts.

Key words: vinylalkoxysilanes; fluoroalkene; radical; ESR.

The structure of the polymers formed by the radical polymerization of vinylsilanes $CH_2=CH-Si-R^1R^2_2$ (R^1 = Me; R^2 = MeO, EtO, Pr^nO, Pr^iO) has been studied previously[1-3] by NMR spectroscopy. The data obtained on the structure of the fragments of the polymer chains (**A**, **B**) of polyvinylsilanes make it possible to assume that the reaction of vinylalkoxysilanes (VAS) with an initiating radical involves abstraction of a H atom from the alkoxy group of VAS resulting in a primary radical, the addition of which at the double bond of VAS produces a new radical. The secondary radical can either add to the double bond of the next VAS molecule or participate in chain transfer by the abstraction of H from the alkoxy group according to Scheme 1.

Scheme 1



In the present work the structure of primary radicals and the process of their addition to branched fluoroalkenes have been studied by ESR in order to establish the possibility of the radical copolymerization of VAS. The UV irradiation of 10 % solutions of methylvinyldi-

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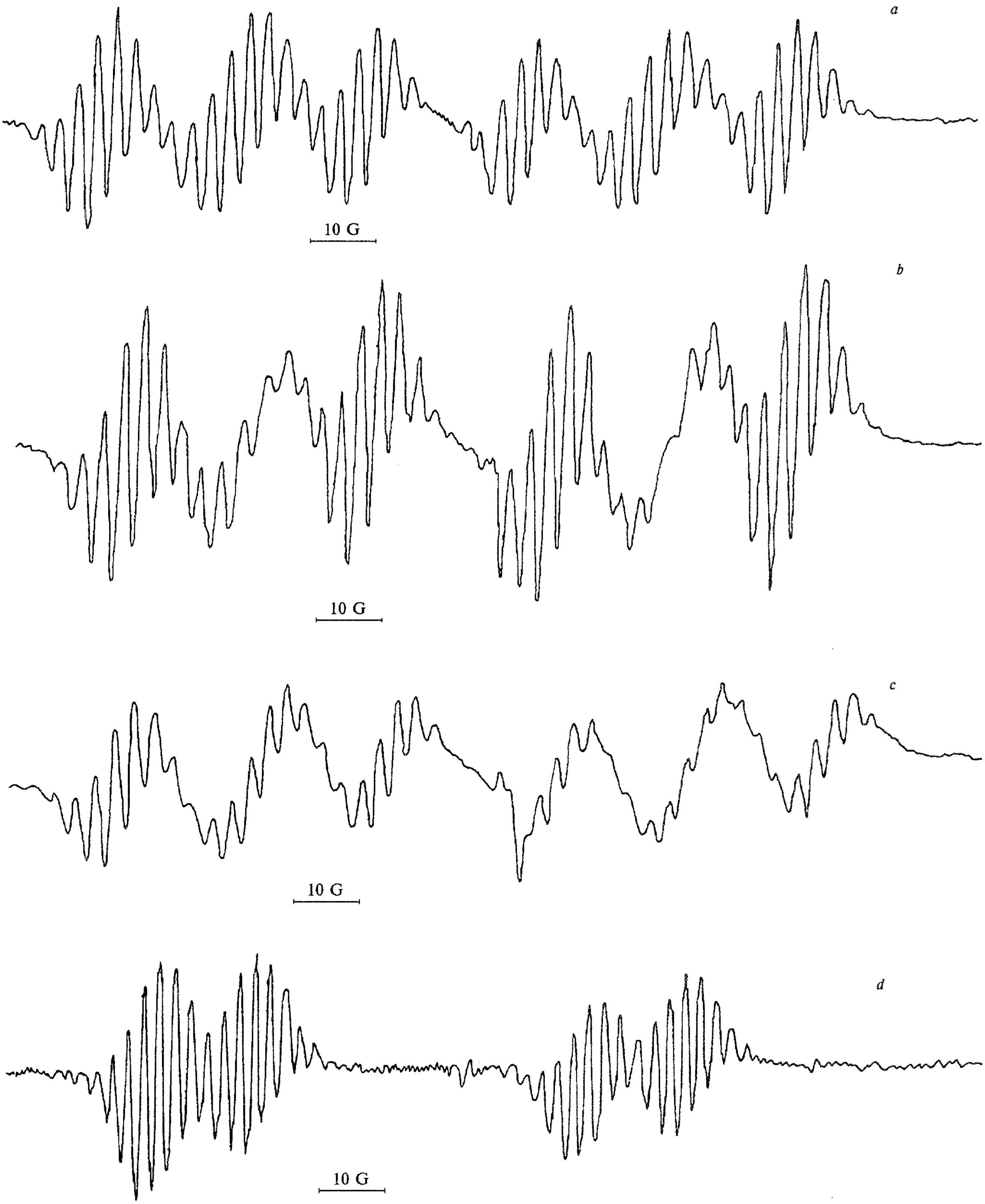
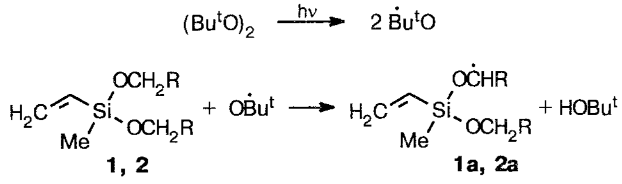


Fig. 1. ESR spectra of radicals: *a*, **3a** at 300 K; *b*, **4a** at 300 K; *c*, **4a** at 260 K; *d*, **5a** at 300 K.

methoxysilane (**1**) and methylvinyldiethoxysilane (**2**) in di-*tert*-butyl peroxide (TBP) at −10÷−20 °C in the resonator of an ESR spectrometer results in primary radicals according to Scheme 2.

Scheme 2

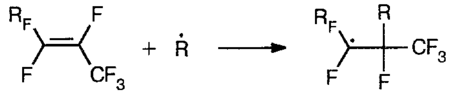


1: R = H
2: R = Me

The ESR spectrum of radical **1a** is characterized by the interaction of the unpaired electron with two equivalent protons, with a the coupling constant of a_H = 19.1 G. The unpaired electron in radical **2a** interacts with three β-protons of the methyl group (a_H = 23 G) and one α-proton (a_H = 17.5 G). The differences between the spectra of radicals **1a** and **2a** indicate that the initiating radical produced from the peroxide abstracts a H atom from the akoxyl groups rather than from the methyl group.

In order to investigate the reactivity of radicals **1a** and **2a**, their reaction with internal fluoroolefins[4,5] was studied. When radicals **1a** or **2a** are generated in the presence of fluoroolefins, the adducts are formed according to Scheme 3.

Scheme 3



3a–6a

3a: $R_F = CF(CF_3)_2$ ($\dot{R}$ = **1a**)
4a: $R_F = CF(CF_3)_2$ ($\dot{R}$ = **2a**)
5a: $R_F = C(CF_3)_3$ ($\dot{R}$ = **1a**)
6a: $R_F = C(CF_3)_3$ ($\dot{R}$ = **2a**)

The ESR spectrum of radical **3a** (Fig. 1, *a*) is characterized by the following coupling constants with the fluorine α-, β-, and γ-atoms: $a_{\text{F-}\alpha}$ = 62.5, $a_{\text{F-}\beta}$(2 F) = 21.7, $a_{\text{F-}\gamma}$(9 F) = 2.7 G. The intensity ratio of the lines in the triplet produced by the nuclei of the two fluorine β-atoms is 1 : 1 : 1 at 20 °C. This indicates an insufficiently high rate of transformations between the forms with C—F-β bonds having nonequivalent positions relative to the $2p_z$-orbital of the unpaired electron.

The ESR spectrum of radical **4a** (Fig. 1, *b*) has $a_{\text{F-}\alpha}$ = 61.2, $a_{\text{F-}\beta}$(2 F) = 17.0, $a_{\text{F-}\gamma}$(9 F) = 2.7 G. The central component of the triplet is broadened, and its intensity increases as the temperature is decreased (Fig. 1, *c*), *i.e.*, the stable conformation (**4a**) has equivalent positions of the fluorine β-atoms relative to the $2p_z$-orbital. The ESR spectra of radicals **5a** and **6a** (Fig. 1, *d*) are characterized by the following constants: **5a**, $a_{\text{F-}\alpha}$ = 60.0, $a_{\text{F-}\beta}$ = 13.0, $a_{\text{F-}\gamma}$ = 2.0; **6a**, $a_{\text{F-}\alpha}$ = 59.5, $a_{\text{F-}\beta}$ = 10.0, $a_{\text{F-}\gamma}$(12 F) = 2.0 G.

When the irradiation is stopped, radicals **3a**—**6a** decay at 20 °C by abstracting H atoms from the original vinylsilanes.[4] It is evident from the above that the radical addition of vinylsilane to branched fluoroolefins can serve as a method for introducing fluorinated substituents into molecules of the former.

Experimental

ESR spectra of the samples were recorded on a Varian E12A radio-frequency spectrometer in evacuated quartz ampules at the ratio perfluoroalkene : vinylsilane : TBP = 10 : 1 : 0.1. Irradiation was performed by focused UV light from a DPSh-1000 lamp. Thermostatting was performed with a UNJPAN-660 system.

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