The ESR study of reactivity of perfluoroacetyldiisopropylmethyl radical

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The kinetics of hydrogen abstraction from hydrocarbons by the air-stable perfluoroacetyldiisopropylmethyl radical was studied by ESR, and a reaction mechanism was proposed. The degree of delocalization of the unpaired electron in the model $C(5)F_3-C(1)^{\cdot}[C(2)(O(4))C(3)F_3]C(6)F_3$ radical was calculated by the MNDO/PM3 method in the UHF approximation. For the conformation in which the CO group lies in the plane passing through the C(1), C(2), and C(5) atoms, the electron density on the O atom is 0.22.

Key words: stable radicals, ESR, fluorine, reactivity, MNDO/PM3 method.

Previously,[1] it has been shown that CsF eliminates the SO_2F_2 fragment from the stable fluorosulfonyloxytetrafluoroethylbis(perfluoroisopropyl)methyl radical $[(CF_3)_2CF]_2C^{\cdot}-CF(CF_3)OSO_2F$ to form a new air-stable $[(CF_3)_2CF]_2C^{\cdot}-C(O)CF_3$ radical (**1**). This is the first example of a stable radical containing a keto group in the β-position with respect to the radical center. The structure of radical **1** suggests the possibility of delocalization of the unpaired electron in the heteroallylic triad. In this work, the degree of delocalization of the unpaired electron in this heteroallylic system was calculated by the MNDO/PM3 method and an ESR study of the reactivity of radical **1** was performed.

Results and Discussion

Quantum-chemical calculations of the spin density distribution in the model perfluoroacetyldimethylmethyl radical $C(5)F3-C(1)^{\cdot}[C(2)(O(4))C(3)F_3]C(6)F_3$ (**2**) were carried out by the MNDO/PM3 method in the UHF approximation.[2] It was established that there are two local minima on the potential energy surface (PES) of this radical corresponding to conformers **2a** and **2b** (Fig. 1). Their energetic, geometric, and electron characteristics are listed in Table 1. The energy of **2a** is 0.9 kcal mol^{-1} less than that of **2b**. In conformer **2a**, in which the carbonyl group is perpendicular to the radical plane, the spin density is nearly completely localized on the C(1) atom, whereas it is partly delocalized on the O and C(2) atoms in conformer **2b** (see Table 1). At the same time, both conformers have almost identical distributions of effective charges. The ionization potentials of **2a** and **2b** are close; however, conformer **2b** has the higher electron affinity. The negative charge in the anions is localized mainly on the C(1) atom. The eigenvalue of the $<S^2>$ operator for the radicals is somewhat overestimated and is close to 0.75. Thus, it follows from the data of quantum-chemical calculations that the spin density on the oxygen atom in conformation **2a** and **2b** is −0.03 and 0.22, respectively. Hence, in the case of free rotation of the acyl group, the average value of the density of the unpaired electron on the oxygen atom will be 0.1.

Since acceptor properties of the fluorine atom and CF_3 group are close, the replacement of two fluorine atoms in each of the two CF_3 groups by two CF_3 groups

Table 1. Heats of formation (ΔH_f/kcal mol^{-1}), ionization potentials (IP/eV), electron affinities (E_a/eV), bond lengths (d/Å), bond orders (W/au), effective atomic charges (q/au), and spin density (ρ/au) for conformers **2a** and **2b** calculated by the MNDO/PM3-UHF method

Conformer	$<S^2>$	$-\Delta H_f$	IP (E_a)	d/Å (W/au)					q/au (ρ/au)					
				C(1)-C(2)	C(2)-C(3)	C(2)-O(4)	C(1)-C(5)	C(1)-C(6)	C(1)	C(2)	C(3)	O(4)	C(5)	C(6)
2a	0.769	466.3	12.9	1.482	1.586	1.200	1.530	1.530	−0.24	0.27	0.32	−0.15	0.42	0.42
			(4.0)	(0.915)	(0.836)	(2.034)	(0.919)	(0.919)	(1.15)	(−0.08)	(0.01)	(−0.03)	(−0.07)	(−0.07)
2b	0.788	465.4	13.0	1.470	1.583	1.214	1.533	1.539	−0.21	025	0.33	−0.16	0.41	0.41
			(4.4)	(0.980)	(0.852)	(1.938)	(0.923)	(0.921)	(1.09)	(−0.21)	(0.00)	(0.22)	(−0.07)	(−0.07)

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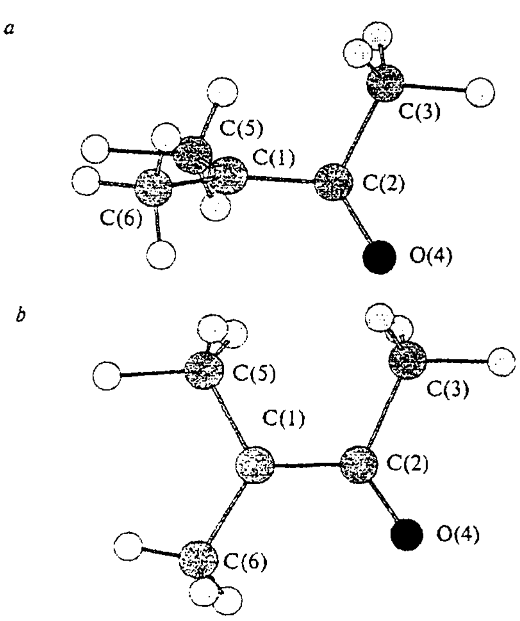

Fig. 1. The structure of conformers **2a** (*a*) and **2b** (*b*) according to the data of quantum-chemical calculations.

in the model radical **2** must not result in a considerable change in the spin density distribution in radical **1**. If so, then the reaction center of the ketoradical **1** might appear on the oxygen atom capable of participation in radical reactions. To prove the above assumptions, the reaction of abstraction of the hydrogen atom characteristic of O-centered radicals[3] was chosen as a model reaction.

To determine the temperature interval in which kinetic characteristics of the reaction of abstraction of the hydrogen atom from hydrocarbons by radical **1** can be measured, thermal stability of the radical was first studied. It was established that decomposition of **1** becomes appreciable at temperatures above 370 K and the energy of activation of decomposition (E_a) was 30.0 kcal mol^{-1}. Decomposition of **1** occurs through β-scission, leading to formation of the $^{\bullet}CF_3$ radical. This is confirmed by the ESR spectrum of the perfluorotriisopropylmethyl radical recorded during thermolysis of **1** in a solution of $[(CF_3)_2CF]_2C{=}CFCF_3$ (*cf.* Ref. 4).

$$\mathbf{1} \xrightarrow{\Delta} (CF_3)_2CF[CF_3(O)C]C{=}CFCF_3 + {}^{\bullet}CF_3$$

$$[(CF_3)_2CF]C{=}CFCF_3 + {}^{\bullet}CF_3 \longrightarrow [(CF_3)_2CF]_3C^{\bullet}$$

It turned out that unlike the carbon-centered perfluorodiisopropylmethyl and perfluorotriisopropylmethyl radicals (stable under these conditions), the air-stable radical **1** appeared to be highly reactive in the reactions of hydrogen abstraction from hydrocarbons of fatty and fatty-aromatic series. For instance, the intensity of the ESR signal of ketoradical **1** in cyclohexane becomes halved over a period of 4.5 min even at 280 K (Fig. 2, *a*). The semilogarithmic anamorphoses of the curves of the loss of radical **1** in cyclohexane at different temperatures are shown in Fig. 2, *b*. Since the solubility of ketoradical **1** in hydrocarbons is limited and the limiting concentration of **1**, according to the ESR data, is equal to ~10^{-3} mol L^{-1}, it can be assumed that the reaction follows a pseudo first order.

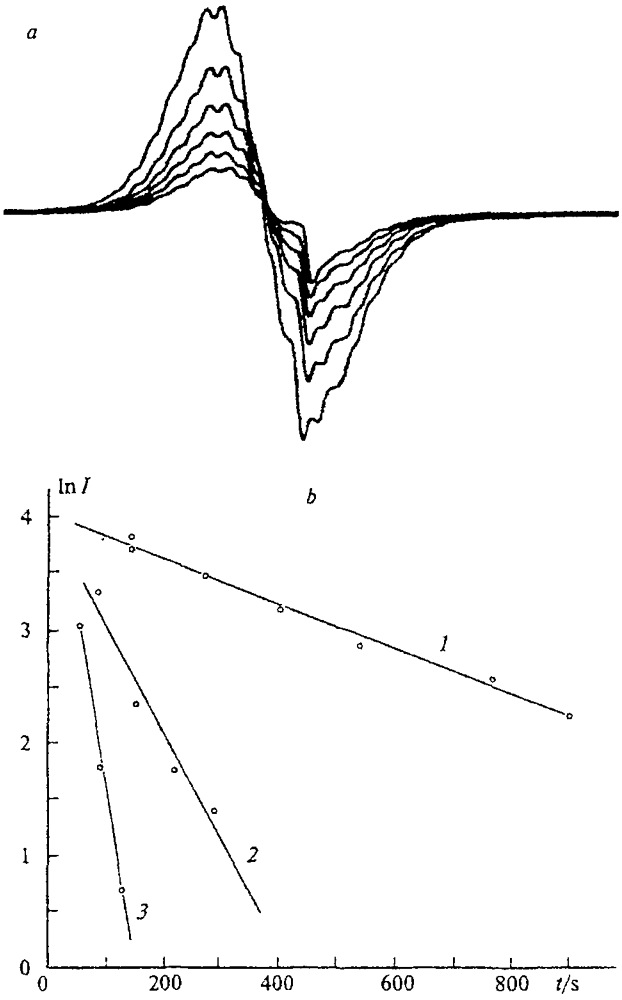

Fig. 2. *a*. Dependence of the intensity of the ESR spectrum of radical **1** on time (recorded at intervals of 132 s) in cyclohexane at 280 K. *b*. Semilogarithmic anamorphoses of curves of loss of radical **1** in cyclohexane at different temperatures: 280 (*1*), 320 (*2*), and 340 K (*3*).

The analysis of the kinetic and thermodynamic data obtained makes it possible to reveal the following characteristic features (Table 2). The rate of abstraction of the hydrogen atom from cyclohexane is several times higher than that of abstraction from hexane. This is explained by the increased number of secondary hydrogen atoms bonded to carbon atoms weaker than the primary hydrogen atoms (provided that the energies of activation of these processes are close). The increased rate of hydrogen abstraction on going to cyclohexene and toluene is caused by the formation of resonance-stabilized allylic and benzyl radicals. The energy of activation of abstraction of a hydrogen atom is drastically increased on going from hexane to decane and octane; this is most likely associated with steric hindrances. It is possible that bulky perfluoroisopropyl groups prevent the long hydrocarbon molecule from approaching the oxygen atom in such a way that the hydrogen atoms are abstracted from secondary carbon atoms, and the ketoradical attacks the terminal atoms of long hydrocarbon molecules.

The kinetic isotopic effect was studied using the interaction of ketoradical **1** with deuterated toluene and cyclohexane as an example.

Reagent	k_H/k_D
Cyclohexane—cyclohexane-d_{12}	3.5
Toluene—toluene-d_8	2.1

The low k_H/k_D value indicates the asymmetry of the transition state in the reaction of H (D) abstraction.[5]

The rate of abstraction of the hydrogen atom is sharply decreased as the electronegative F atom in ketoradical **1** is replaced by the methyl group exhibiting donor properties. The new radical **4** was obtained by addition of the methyl radical to vinyl ketone **3**:

$$\underset{\mathbf{3}}{(CF_3)_2C{=}C[C(O)CF_3]CF(CF_3)_2} + {}^{\cdot}CH_3 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{4}}{CH_3(CF_3)_2C{-}{}^{\cdot}C[C(O)CF_3]CF(CF_3)_2}$$

Table 2. Kinetic and thermodynamic data of abstraction of the hydrogen atom from hydrocarbons (RH) by α-ketoradical **1**

RH	$k \cdot 10^3$/mol^{-1} L s^{-1} (T/K)	E_a/kcal mol^{-1}
Toluene	6.5 (240); 15.0 (260); 53.7 (280); 134.0 (300)	6.3
Toluene-d_8	2.1 (240); 5.1 (260); 17.9 (280); 65.0 (300)	8.3
Hexane	1.6 (280); 5.2 (290); 8.17 (300); 10.3 (10.3)	10.0
Cyclohexane	19.5 (280); 34.2 (300); 87.9 (320); 275 (340)	8.1
Cyclohexane-d_{12}	9.9 (300); 22 (320); 48 (340); 122 (360)	9.0
Cyclohexene	30 (240); 59 (250); 74 (260)	5.6
Heptane	3.6 (270); 10.4 (290); 48.1 (320); 75.7 (340)	7.8
Octane	3.4 (300); 5.2 (320); 35 (330); 74 (340); 126 (350)	16.5

The methyl radicals were generated both from *tert*-butylperoxide and by iodine abstraction from methyl iodide by boron-centered carboranyl radicals obtained in the photolysis of dicarboranylmercury.[6] In both cases, identical ESR spectra of radical **4** were observed.

The loss of radical **4** in hydrocarbons becomes noticeable only at temperatures above 340 K. From this it follows that the rate of abstraction of the hydrogen atom by heteroallylic ketoradicals depends on the acceptor properties of these radicals (*cf.* Refs. 7 and 8).

It should be noted that the hydrocarbon radicals formed in the course of the reaction of hydrogen abstraction are capable of addition to the oxygen atom of the ketoradical to give the corresponding ethers, which was proved by studying the reaction mixtures by chromato-mass spectrometry. Thus, for instance, the formation of vinyl ether **5b** was detected in the cyclohexane—ketoradical **1**:

$$\mathbf{1} + cyclo\text{-}C_6H_{12} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{5a}}{[(CF_3)_2CF]_2C{=}C(CF_3)OH} + cyclo\text{-}{}^{\cdot}C_6H_{11}$$

$$\mathbf{1} + cyclo\text{-}{}^{\cdot}C_6H_{11} \longrightarrow \underset{\mathbf{5b}}{[(CF_3)_2CF]_2C{=}C(CF_3)OC_6H_{11}}$$

The validity of this scheme is also confirmed by the ESR spectral data. The loss of ketoradical **1** in solutions of hydrocarbons is accompanied by generation of new stable radicals which are the spin-adducts of enol **5a** or vinyl ethers **5b,c**, and hydrocarbon alkyl radicals:

$$\mathbf{1} + HR \longrightarrow {}^{\cdot}R$$

$$[(CF_3)_2CF]_2C{=}C(CF_3)OX + {}^{\cdot}R \longrightarrow$$

$$\longrightarrow [(CF_3)_2CF]_2C^{\cdot}{-}CR(CF_3)OX,$$

5a: X = H
5c: X= Alk

If radical **1** interacts with $BH_3 \cdot NMe_3$ or $HP(O)(OPr^i)_2$, the hyperfine interaction (HFI) of the unpaired electron with the ^{11}B and ^{31}P nuclei (a_B = 15.0 and a_P = 60.0 Gs) is recorded in the ESR spectrum of the stable radical. The magnetic nonequivalence of the fluorine nuclei in the new stable radicals does not allow a complete interpretation of their ESR spectra.

Thus, air-stable perfluorinated heteroallylic α-ketoradicals have been shown to be capable of abstraction of the hydrogen atom from hydrocarbons: a mechanism for the reactions studied was suggested and the kinetic parameters of reactions studied were determined. The rate of reactions of this type is dependent on the acceptor properties of ketoradicals.

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Mass spectra were recorded on a VG-7070E chromato-mass spectrometer (70 eV).

The solvents (see Table 2) were purified according to standard procedures.[9] Deuterated solvents were used as received.

Kinetic measurements of abstraction of the hydrogen atom from hydrocarbons by radical 1. Ketoradical **1** (5 vol.%) was added into an ampule containing a hydrogen donor. The solution was stirred and placed in the thermostatting system of the ESR spectrometer equipped with a Unipan electronic temperature controller. Since the solubility of perfluoroorganic compounds in hydrocarbons is low, an appreciable portion of the ketoradical remained at the bottom of the ampule. The ampule was set in such a way that the ketoradical is outside of the resonant cavity. A solution of the ketoradical in the hydrocarbon was monitored; according to the data obtained, the concentration of the solution was 10^{-3} to 10^{-4} mol L^{-1}. Further, dependences of the intensity of the ESR spectra of ketoradical **1** on time were recorded at different temperatures (Fig. 2, *a*). The obtained kinetic curves were rectified in a semilogarithmic anamorphosis (Fig. 2, *b*). The values of the rate constants of hydrogen abstraction were determined from the obtained $\ln I(t)$ dependences.

Chromato-mass-spectrometric determination of the products of interaction of radical 1 with cyclohexane. A mixture of radical **1** (0.15 mL) and cyclohexane (0.15 mL) was kept in a sealed ampule at 300 K for 30 min with regular shaking. After completion of the reaction (disappearance of the dark brown color of radical **1**), the mixture was analyzed by chromato-mass spectrometry.

Mass spectrum of the adduct of radical **1** and cyclohexane **5b** (*m/z*): 529 [M−H], 359 [$C_8F_{13}O$], 309 [$C_7F_{11}O$], 83 [C_6H_{11}], and 69 [CF_3].

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