The ESR study of the structure and reactivity of α-ketoradicals, derivatives of $(CF_3)_3CC(O)C(O)CF_3$

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The structure and reactivity of α-ketoradicals, derivatives of $(CF_3)_3CC(O)C(O)CF_3$ (**1**), were studied by ESR spectroscopy. The photoreduction of α-diketone **1** in a solution of cyclohexane in perfluorodipentyl ether results in the formation of radicals of two types, $(CF_3)_3CC(2)(O(4))^{\cdot}C(3)(O(6)H)CF_3$ (**1a**) and $(CF_3)_3C^{\cdot}C(OH)C(O)CF_3$ (**1b**) in a ~40 : 1 ratio. The degree of delocalization of the spin density in two conformers of radical **1a** was calculated by the MNDO/PM3 method in the UHF approximation. It was established that radicals **1a** and **1b** are capable of reversible dimerization. The rate constant of dimerization and the enthalpy of the radical—dimer equilibrium were measured for radical **1a**. A decrease in the rate of dimerization of radical **1a** upon addition of complexing solvents ($(CF_3)_3COH$ and p-$CF_3C_6H_4CF_3$) was found. The influence of the solvents on the rate of dimerization was also detected for α-ketoradical $(CF_3)_3CC(O)^{\cdot}C(OSiMe_2Ph)CF_3$ (**1c**).

Key words: ESR spectroscopy; α-ketoradical, reversible dimerization; perfluorinated α-diketones, photoreduction, spin-adduct.

Allylic radicals are known to be more thermodynamically stable than alkyl radicals. However, many of them possess a higher reactivity as compared to saturated radicals.[1] As usual, it is related to delocalization of the unpaired electron, due to which a portion of the electron density can be transferred to a less shielded atom. Previously,[2] we have shown that unlike its alkyl analogs, $[(CF_3)_2CF]_2{}^{\cdot}CCF_2CF_3$, *etc.*, the stable heteroallylic α-ketoradical $[(CF_3)_2CF]_2{}^{\cdot}CC(O)CF_3$ is capable of abstracting the H atom from alkenes. This is associated with nonuniform distribution of the density of the unpaired electron between the atoms of allylic triad in heteroallylic radicals containing the carbonyl group in α position with respect to the radical center. Thus, 2-alkanonyl radicals can be thought of as a resonance hybrid of two allylic structures, $RR'^{\cdot}CCORR''$ and $RR'C{=}C^{\cdot}ORR''$, taken in the 6 : 1 ratio.[3]

The degree of delocalization of the unpaired electron in the model $C(1)F_3{-}C(2)^{\cdot}[C(3)(O)CF_3]CF_3$ radical has been calculated by the MNDO/PM3 in the UHF approximation.[2] It has been shown that in the case of conformation with the carbonyl group lying in the plane passing through the C(1), C(2), and C(3) atoms, the density of the unpaired electron on the O atom is equal to 0.22. If the carbonyl group lies perpendicular to the above plane, then the density on the O atom is equal to 0, and the latter conformation is energetically favorable (by 1.5 kcal mol^{-1}). Obviously, the equilibrium between the conformers with different positions of the carbonyl group with respect to the axis of the $2p_z$ orbital of the unpaired electron can be dependent on the structure of the substituents in these radicals.

In this work we studied the ESR spectra and reactivity of heteroallylic radicals, derivatives of α-diketone $(CF_3)_3CC(O)C(O)CF_3$ (**1**), which are less shielded as compared to the perfluoroacetyldiisopropylmethyl radical.

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer in degassed quartz ampules. The samples were irradiated by a focussed light of a DRSh-1000 lamp and thermostatted using a Unipan electronic temperature controller.

To obtain kinetic curves, the magnitudes of magnetic field were set equal to those corresponding to the maxima of the absorption signals, and after switching off the light the dependences of the intensities of the ESR signals on time were recorded. The concentrations for kinetic calculations were determined analogously to the procedure described previously;[4] a toluene solution of 2,2,6,6-tetramethylpiperidine-*N*-oxyl ($1.5 \cdot 10^{-3}$ mol L^{-1}) was used as a standard. α-Diketone **1** was synthesized according to the known procedure.[5]

Results and Discussion

Radicals of two types are recorded by the ESR method in the photoreduction of compound **1** in perfluorodipentyl ether with addition of cyclohexane (~3% by volume) (Fig. 1). These radicals are characterized by the following constants of hyperfine interaction (HFI) at 300 K: **1a**, $a_F(3\ F) = 14.7$ G, $a_F(9\ F) =$

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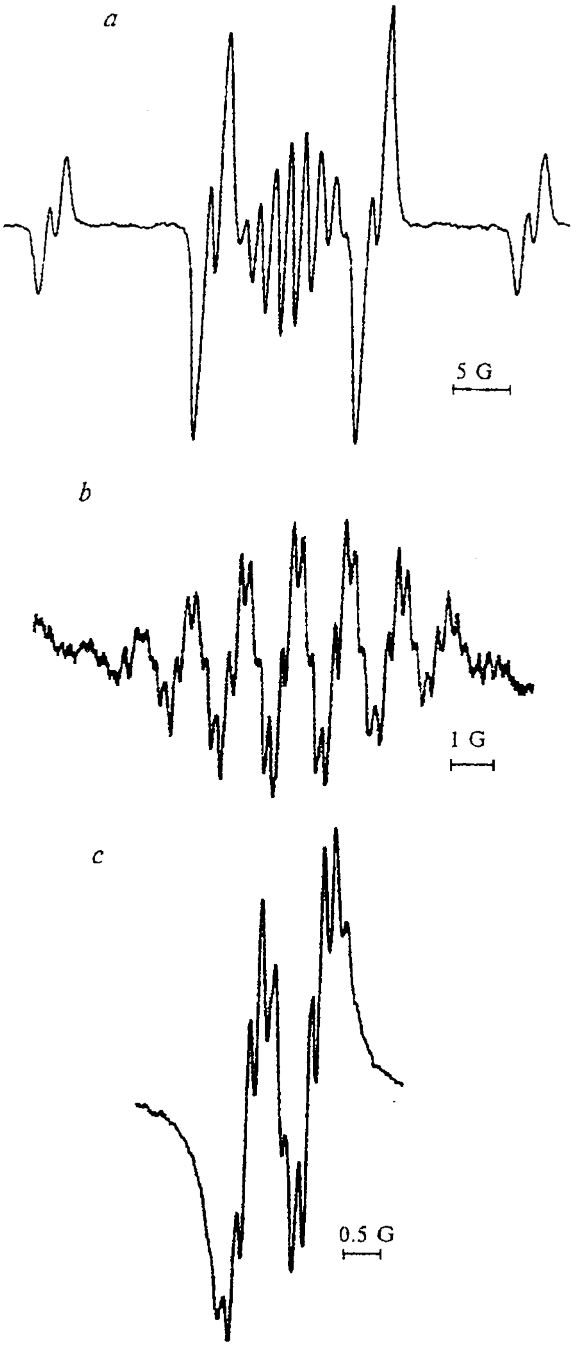
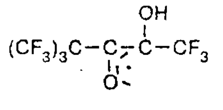


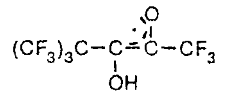
Fig. 1. *a*. The ESR spectrum of radicals **1a,b** at 300 K, the amplitude of low-frequency modulation is 0.8 G.
b. The ESR spectrum of radicals **1b** at the amplitude of modulation of 0.1 G.
c. The low-field component of the ESR spectrum of radical **1a** at the amplitude of modulation of 0.1 G.

0.175 G, and a_H = 0.85 G; **1b**, a_F(3 F) = 0.25 G, a_F(9 F) = 1.3 G. On the basis of these data, the following structures can be assigned to the radicals observed:



$(CF_3)_3C{-}C(O^{\cdot}){=}C(OH){-}CF_3$

1a



$(CF_3)_3C{-}C(OH){=}C(O^{\cdot}){-}CF_3$

1b

No HFI with the nucleus of the H atom is detected in the ESR spectrum of radical **1b**, since this atom is likely located close to the plane perpendicular to the axis of the $2p_z$ orbital of the unpaired electron (*cf.* Ref. 6).

The doublet splitting caused by the proton in the spectrum of radical **1a** disappears upon photoreduction of compound **1** in perfluorodipentyl ether with addition of deuterated cyclohexane. This can prove the existence of structure **1a**.

To clarify specific features of the electronic structure of radical **1a**, we performed quantum-chemical calculations by the MNDO/PM3 method[7] in the UHF approximation. There are two local minima on the potential energy surface of radical **1a** corresponding to two conformers. In the first conformer (**1a′**), the carbonyl group is perpendicular to the C(2)C(3)O(6) plane (ΔH_f = −671.4 kcal mol^{-1}), while in the second conformer (**1a″**) it lies in the plane mentioned above (ΔH_f = −672.3 kcal mol^{-1}).

In conformer **1a′**, whose energy is 0.9 kcal mol^{-1} higher than that of **1a″**, the spin density is almost completely localized on the C(3) atom (0.92), while it is equal to 0.15 and only to 0.02 on the O(6) and O(4) atoms, respectively. In radical **1a″**, the density of the unpaired electron is partly transferred to the O(4) and C(2) atoms (0.18 and −0.15, respectively). At the same time, the distribution of the effective charges in both conformers is nearly the same. The ionization potentials of radicals **1a′** and **1a″** are close, but the electron affinity is somewhat higher for conformer **1a″** (Tables 1 and 2, Fig. 2).

Thus, the calculations showed that spin-adduct **1a** is a resonance hybrid of two allylic structures, $CF_3(OH)C^{\cdot}COC(CF_3)_3$ and $CF_3(OH)C{=}CO^{\cdot}C(CF_3)_3$,

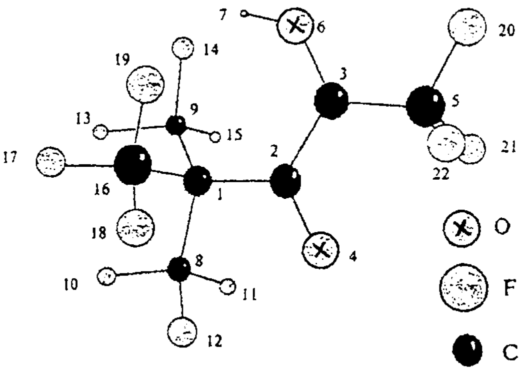


Fig. 2. The structure of radical **1a″** according to the data of quantum-chemical calculations.

Table 1. Heats of formation (ΔH_f), ionization potentials (*IP*), eigenvalues of operator S^2 ($<S^2>$), bond lenghts (*d*), and bond orders (*W*) for conformers **1a**″ and **1a**′ (method MNDO/PM3-UHF)

Radical	$-\Delta H_f$ /kcal mol^{-1}	*IP* /eV	$<S^2>$	*d*/Å (*W*/au)					
				C(1)—C(2)	C(2)—(3)	C(2)—O(4)	C(3)—C(5)	C(3)—O(6)	C(1)—C(8)
1a″	672.3	10.93	0.772	1.553 (0.875)	1.475 (0.977)	1.214 (1.932)	1.547 (0.905)	1.324 (1.162)	1.584 (0.910)
1a′	671.4	11.04	0.760	1.548 (0.879)	1.493 (0.906)	1.205 (2.016)	1.540 (0.904)	1.330 (1.141)	1.523 (0.910)

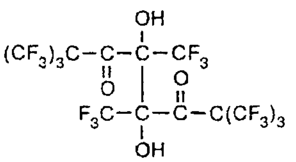
Table 2. Effective charge on atoms (*q*) and spin density (ρ) for conformers **1a**″ and **1a**′ (method MNDO/PM3-UHF)

Radical	Atom	*q*/au	ρ/au				ρ_Σ /au
			s	p_x	p_y	p_z	
1a″	C(1)	−0.27					
	C(2)	0.29	−0.02	−0.01	−0.03	−0.09	−0.15
	C(3)	−0.17	0.06	0.13	0.08	0.57	0.84
	O(4)	−0.20	0.00	0.00	0.00	0.18	0.18
	C(5)	0.43	−0.01	−0.03	−0.01	−0.01	−0.06
	O(6)	−0.12	−0.00	0.04	−0.01	0.14	0.17
	H(7)	0.23					
	C(8)	0.39					
	C(9)	0.38					
1a′	C(1)	−0.27					
	C(2)	0.31	−0.01	−0.01	−0.02	−0.01	−0.05
	C(3)	−0.20	0.08	0.52	0.27	0.05	0.92
	O(4)	−0.18	0.00	0.00	0.01	0.01	0.02
	C(5)	0.43	−0.01	−0.01	0.00	−0.02	−0.04
	O(6)	−0.10	0.00	0.12	0.04	−0.01	0.15
	H(7)	0.22					
	C(8)	0.39					
	C(9)	0.39					

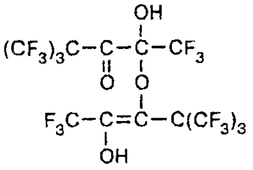
and that the contribution of the latter can be very important from the chemical point of view.

The species under study are unstable, and radicals **1a** and **1b** disappear after switching off the UV irradiation of a solution of α-diketone **1** in perfluorodipentyl ether (with addition of 2—3 vol.% of cyclohexane whose solubility in this ether is low) in the temperature interval from 240 to 280 K. However, the rates of their decay are different: 1 min for radical **1a** and several seconds for radical **1b**. Heating of the non-irradiated sample to 300 to 340 K after photolyzing it for 15 to 20 min results in the appearance of the ESR spectrum of radicals **1a** and **1b**, whose intensity increases as the temperature increases. This is evidence that the main channel of the decay of the radicals is their reversible dimerization. The enthalpy of the radical—dimer equilibrium was estimated from the temperature dependence of the concentration of radical **1a**: ΔH = 15.5±1.5 kcal mol^{-1}.

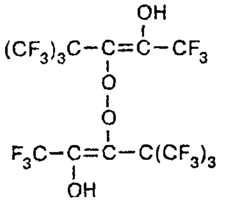
Three plausible structures of dimers formed can be proposed:



A



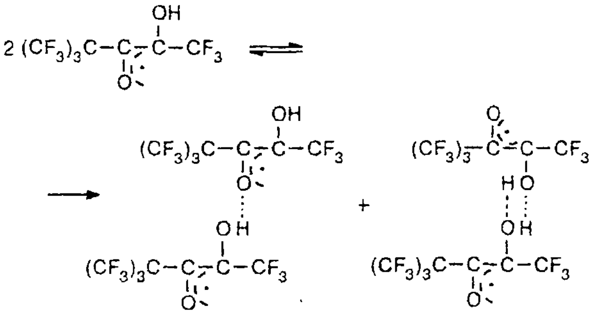
B



C

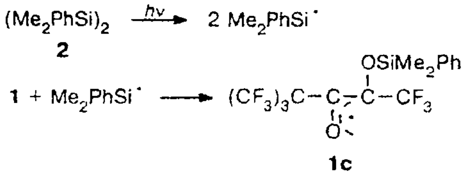
It is known that the rate of dimerization depends on the degree of shielding of the reaction center.[8] In heteroallylic radical **1a**, the carbon radical center C(3) is much less shielded and the oxygen radical center is more shielded than those in radical **1b**. Since the rate of dimerization of radical **1a** is much lower than that of **1b**, it can be assumed that the dimer is formed due to the reaction center on the O atom and, hence, it has structure **B** or **C**. The fact that the stable α-ketoradical $[(CF_3)_2CF]^{\cdot}CC(O)CF_3$ is not dimerized with the formation of the O—O bond[2] is evidence in favor of structure **B**.

The study of the dimerization kinetics of radical **1a** in perfluorodipentyl ether in the temperature interval from 240 to 280 K showed that the curve of decay of **1a** consists of two portions, fast (1—3 s) and slow portions (~30 s). It can be assumed that the fast portion of the kinetic curve is associated with the cross-recombination of radicals **1a** and **1b**, while the slow portion is associated with dimerization of **1a**. The rate constant of dimerization (2*k*) of radical **1a** measured along the slow portion of the kinetic curve equals $7 \cdot 10^3$ L mol^{-1} s^{-1} and is temperature-independent within the limits of measurement (±20%). The observed rate constant of dimerization of radicals **1a** is approximately an order of magnitude lower than those for fluoroorganic radicals with close values of the molecular weights.[8] This can be associated with the low density (~0.2) of the unpaired electron on the O atom, which results in increasing the localization energy and requires a closer approach between the radicals for overlapping the orbitals and the formation of the O—O or O—C bond. The self-association of the radicals or the formation of complexes between radical **1a** and traces of hydrated α-diketone due to hydrogen bonds, which decreases translational and rotational diffusion of the radicals, can also favor the decrease in the rate of dimerization.



To test the latter assumption, we studied the effect of perfluoro-*tert*-butyl alcohol capable of forming hydrogen bonds with both the hydroxyl and the carbonyl groups on the dimerization rate of radical **1a**. In fact, the following values of the effective rate constants of dimerization ($2k$/L mol^{-1} s^{-1}) were obtained for the $(CF_3)_3COH$ concentration of 1 mol L^{-1} at 240, 260, and 280 K: $2k_{240} = 9 \cdot 10^2$, $2k_{260} = 1.9 \cdot 10^3$, and $2k_{280} = 2.5 \cdot 10^3$, while the corresponding values in neat $(CF_3)_3COH$ are equal to $2k_{240} = 1.6 \cdot 10^2$, $2k_{260} = 3.7 \cdot 10^2$, and $2k_{280} = 9.1 \cdot 10^2$, respectively. These data are evidence of the strong effect of the formation of hydrogen bond on the rate of dimerization of radical **1a**. It should also be noted that addition of perfluoro-*tert*-butyl alcohol to the solution under study results in a change in the constants of HFI with the nuclei of fluorine atoms; their values for the alcohol itself are equal to $a_F(3\ F) = 13.25$ G (for **1a**) and $a_F(9\ F) = 1.0$ G (for **1b**). Thus, the change in the HFI constants confirms the formation of complexes between **1a** (or **1b**) and $(CF_3)_3COH$ (*cf.* Ref. 9). We also observed a decrease in the HFI constants in the photochemical generation of radical **1a** in a saturated solution of $Ph_3P{=}O$ in cyclohexane ($a_F(3\ F) = 12.5$ G). The constant of HFI with the F nuclei of the CF_3 group increases to 13.5 G as the temperature increases to 400 K, which also points to the formation of a hydrogen bond between the hydroxyl proton of the radical and the phosphate group.

To compare the effect of coordination of the H atom of the hydroxyl group of the alcohol molecule with the lone electron pair of the oxygen radical center (which is tantamount to an increase in its shielding) and that of the formation of a hydrogen bond between the alcohol molecule and the OH group of the ketoradical resulting in the decrease in translational and rotational diffusion on the reactivity of α-ketoradical, we studied the ESR spectra and reactivity of the spin-adducts of silicon-centered radicals ($^{\bullet}SiPhMe_2$) with α-diketone **1**.



$$(Me_2PhSi)_2 \xrightarrow{h\nu} 2\,Me_2PhSi^{\bullet}$$

The ESR spectrum of radical **1c** (Fig. 3) obtained after irradiation of compounds **2** and **1** in a solution of perfluorodipentyl ether is characterized by the following HFI constants: **1c**, $a_F(3\ F) = 12.5$ G, and $a_F(9\ F) = 0.35$ G. Like **1a** and **1b**, radical **1c** is dimerized after switching off the UV irradiation, which is evidenced by the increase in its steady concentration at heating (310—350 K) in the absence of irradiation. The rate constant of dimerization ($2k$) of radical **1c** in perfluorodipentyl ether in the interval from 240 to 280 K equals to $7.5 \cdot 10^2$ L mol^{-1} s^{-1} and is temperature-independent, as for **1a**. The decrease in the rate constant of dimerization of radical **1c** as compared to the $2k$ value for **1a** in the inert solvent may be related to the fact that the addition of a bulky silicon-centered radical results in increasing the steric shielding of the carbon radical center. The obtained value of the enthalpy of the radical—dimer equilibrium, $\Delta H = 5.5$ kcal mol^{-1}, is an argument in favor of this assumption.

We also studied the effect of complexing solvents on the dimerization rate of radical **1c**. In this case, a sharper decrease in the dimerization rate is observed at the $(CF_3)_3COH$ concentration of 1 mol L^{-1} as compared with radical **1a**: $2k_{240} = 2$, $2k_{260} = 6.5$, and $2k_{280} = 10.6$ L mol^{-1} s^{-1}. From this it follows that

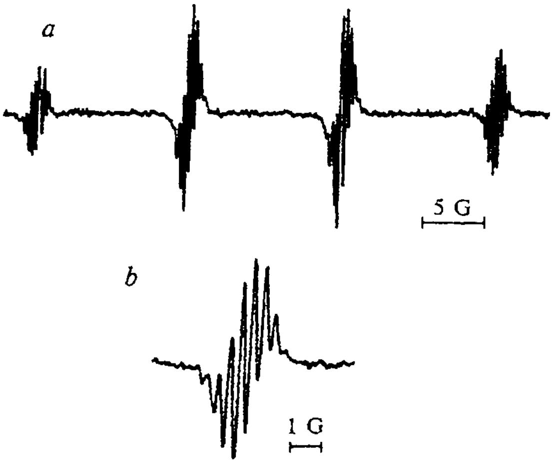


Fig. 3. *a*. The ESR spectrum of radical **1c** at 300 K.
b. The low-field component of the multiplet of the ESR spectrum of radical **1c**.

coordination of the H atom of the hydroxyl group of the alcohol molecule with the lone electron pair of the carbonyl O atom is the main factor decreasing the rate of dimerization of ketoradicals.

To study the effect of the compounds capable of forming π-complexes on the dimerization rate of ketoradicals, we investigated the dimerization kinetics of radical **1c** in p-CF_3—C_6H_4—CF_3 and obtained the following values of the effective rate constants of dimerization ($2k$/L mol^{-1} s^{-1}): $2k_{240} = 9 \cdot 10^1$, $2k_{260} = 1.3 \cdot 10^2$, and $2k_{280} = 2.2 \cdot 10^2$. The decrease in the dimerization rate is not so large as in the case of perfluoro-*tert*-butyl alcohol since p-CF_3—C_6H_4—CF_3 is a weak donor, and ketoradical is scarcely solvated in such a solvent.

Having established that radical **1c** is most stable in perfluoro-*tert*-butyl alcohol and that its concentration amounts to ~10^{-3} mol L^{-1}, we studied the HFI of the unpaired electron with the ^{13}C nuclei in radical **1c** in this solvent. The ESR spectrum of radical **1c**, in which the outermost components of two satellite doublets from the ^{13}C nuclei of the C(3) and C(2) atoms, a(C(3)) = 19.25 G and a(C(2)) = 10.25 G, were recorded at an amplification 100 times larger than that at which the main signal was recorded, is shown in Fig. 4, *a*. The overall intensity of the satellite lines is ~1%, which corresponds to the natural abundance of ^{13}C. The satellites recorded at 270 K at low amplitude modulation make it possible to determine the sign of the spin density on the C(3) and C(2) atoms. The high-field component of the HFI on the C(3) atom is broadened as compared to the low-field component, which indicates the positive spin density. On the contrary, the low-field component of the HFI on the C(2) atom is more broadened than the high-field component (Fig. 4, *b*), and this is characteristic of the negative spin density.[10] The calculations of the HFI constant on the ^{13}C nucleus for the C(3) atom according to the following equation: $a(C(3)) = Q_C\rho_{C(3)} - Q_{C(3;2)}\rho_{C(2)}$,[10] where $Q_C = 35.6$, $Q_{C(3,2)} = 13.9$, $\rho_{C(3)} = 0.57$, and $\rho_{C(2)} = -0.09$ (based on the calculations of the spin density distribution), gave $a(C(3)) = 21.54$ G. The disagreement with the experimental value, $a(C(3)) = 19.25$ G, is likely associated with some inconsistency between the Q_C and $Q_{C(3,2)}$ values and the parameters of fluorinated radicals.

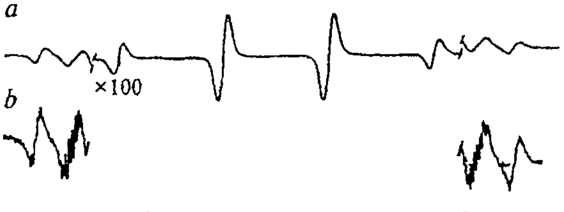
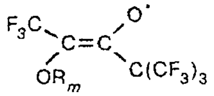


Fig. 4. *a*. The ^{13}C satellites recorded at 300 K and at an amplification 100 times larger than that at which the main signal was recorded; the amplitude of modulation is 0.8 G. *b*. The ^{13}C satellites recorded at 270 K, the amplitude of modulation is 0.2 G.

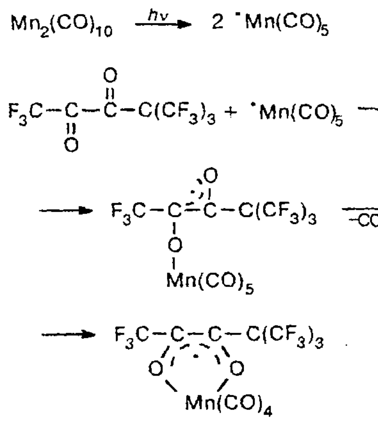
Based on the stabilizing effect of perfluoro-*tert*-butyl alcohol on α-ketoradicals caused by coordination of the hydroxyl group of the alcohol molecule with the lone electron pair of the oxygen radical center, it is possible to propose a method for stabilization of other species of similar structure, for instance, of spin-adducts of metal-centered free radicals with perfluorinated α-diketones:



1d,e

R_m = Mn(CO)$_5$ (**d**), WCp(CO)$_3$ (**e**)

In toluene, it was possible to detect the spin-adducts formed only at temperatures below 240 K (**1d**) and 200 K (**1e**) because of their fast transformation into stable paramagnetic complexes following the reaction of intramolecular oxidation:



If $(CF_3)_3COH$ is used as a solvent, spin-adducts **1d,e** can be observed even at 330 K. This is evidence of stabilization of radicals **1d,e** due to the formation of a hydrogen bond with perfluoro-*tert*-butyl alcohol.

The species obtained in the course of investigation are characterized by the following HFI constants: **1d**, $a_F(3\ F) = 10.75$ G (*cf.* Ref. 11: 12.7 G), and $a_{Mn} = 2$ G (*cf.* Ref. 11: 1.6 G); **1e**, $a_F(3\ F) = 7.75$ G (*cf.* Ref. 11: 12.6 G), and $a_F(9\ F) = 0.5$ G. Changes in the values of the HFI constants in alcohol as compared to those in toluene are also a result of complexation of radicals **1d,e** and $(CF_3)_3COH$.

Thus, α-ketoradicals **1a** and **1b**, derivatives of $(CF_3)_3CC(O)C(O)CF_3$, are capable of reversible dimerization, and addition of such complexing solvents as $(CF_3)_3COH$ and p-$CF_3C_6H_4CF_3$ decreases their reactivity.

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