ESR study of the structure and reactivity of spin-adducts of element- and metal-centered radicals with perfluorinated α-triketones

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The addition of element-centered radicals to perfluorinated α-triketones $(CF_3)_2CFCOCOCOC_2F_5$ (**1**) and $(CF_3)_2CFCOCOCO(CF_3)_2$ (**2**) was studied by the ESR method. In the case of Si-centered radicals, α-siloxydiketomethyl radicals are formed, which are characterized by the highest delocalization of an unpaired electron. The dimerization of these radicals is characterized by a low value of the enthalpy of the radical—dimer equilibrium (2.7 kcal mol^{-1}). The $^{\cdot}Ge(C_6F_5)_3$ and $^{\cdot}Mn(CO)_5$ radicals are added to **1** at the carbonyl group directly bound to the pentafluoroethyl substituent. The hindered rotation of the $(CF_3)_2CF$ group was observed for the spin-adduct of $^{\cdot}Ge(C_6F_5)_3$ with **2**.

Key words: spin-adduct, perfluorinated α-triketones, ESR, heteroallyl radical.

We have shown previously[1,2] that α-ketoradicals, depending on their structure, are capable of abstraction of the hydrogen atom and dimerization. For example, the heteroallylic α-ketoradical $[(CF_3)_2CF]_2{}^{\cdot}CC(O)CF_3$, which is stable in air and in which 20% of the unpaired electron density is localized on the oxygen atom,[1] abstracts the hydrogen atom from hydrocarbons of the aliphatic and aliphatic-aromatic series. Less sterically hindered α-ketoradicals, such as $(CF_3)_3CC(O)^{\cdot}C(OH)CF_3$, are capable of abstraction of the hydrogen atom and dimerization.[2] In this work, we studied the reactions of triketones $(CF_3)_2CFCOCOCOC_2F_5$ (**1**) and $(CF_3)_2CFCOCOCOCF(CF_3)_2$ (**2**) with the element- and metal-centered radicals $^{\cdot}SiMe_2Ph$, $^{\cdot}SiMe_3$, $^{\cdot}Ge(C_6F_5)_3$, $^{\cdot}Mn(CO)_5$, and $^{\cdot}Re(CO)_5$. The presence of three carbonyl groups can result in the formation of ketoradicals with different structures.

Experimental

ESR spectra were recorded on a Varian E-12A instrument in evacuated quartz ampoules. Irradiation was carried out by the focused light of a DRSh-1000 lamp. Samples were thermostatted by an electronic regulator (Unipan).

Results and Discussion

The reaction of the Si-centered radicals with **1** affords two types of spin-adducts in a ratio of ~100 : 1. The first adduct (**1a**) is characterized by the following HFC constants: $a_{\gamma\text{-}F}(2F)$ = 2 G, $a_{\gamma\text{-}F}(1F)$ = 1.2 G (Fig. 1), which indicates that the radical is added to the oxygen atom of the central carbonyl group. In the second adduct (**1b**), the HFC constant with two nuclei of the fluorine atoms of the ethyl group increases sharply and amounts to 15 G; in addition, each line of the triplet is split into a quartet ($a_{\gamma\text{-}F}(3F)$ = 0.9 G) of doublets ($a_{\delta\text{-}F}(1F)$ = 0.3 G) on the fluorine atoms of the trifluoromethyl and perfluoroisopropyl groups. This indicates the addition of the Si-centered radical in this

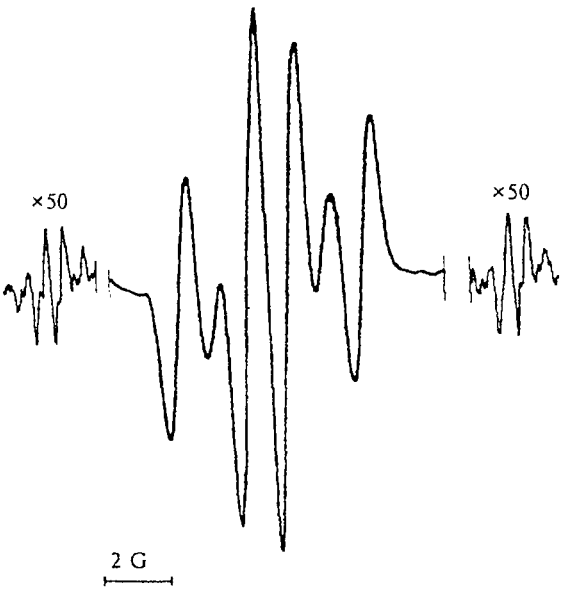

Fig. 1. ESR spectra of spin-adducts **1a,b** at 300 K.

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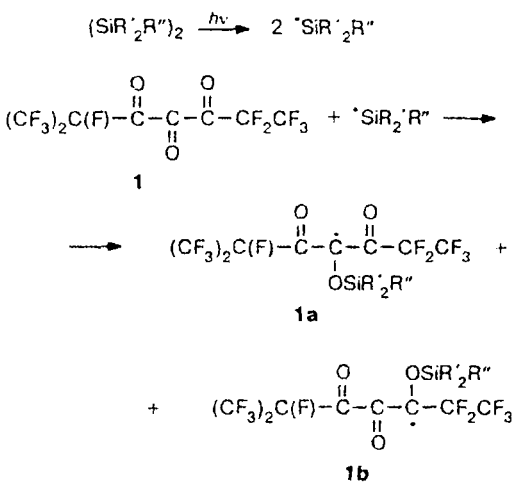
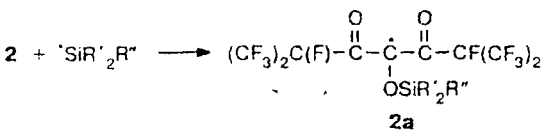
adduct to oxygen of the carbonyl group adjacent to the perfluoroethyl group.



R′ = Me, R″ = Me, Ph

The reaction of the Si-centered radicals with **2** results in the formation of a radical (Fig. 2, *a*), which is characterized by the interaction of the unpaired electron with two equivalent nuclei of the fluorine atoms ($a_{\gamma\text{-}F}(2F)$ = 1.7 G) and nuclei of the fluorine atoms of four trifluoromethyl groups ($a_{\delta\text{-}F}(12F)$ = 0.35 G). These data indicate the addition of the Si-centered radical to the oxygen atom of the central carbonyl group.



We detected the interaction of the unpaired electron with the ^{13}C nucleus (Fig. 2, *b*). The total intensity of satellite lines is ~1%, which corresponds to the isotope content of ^{13}C. The value of the hyperfine coupling constant with the ^{13}C nucleus (a_C = 17.4 G) is lower than that in the $(CF_3)_3CC(O)^{\cdot}C(OH)CF_3$ radical containing one carbonyl group (a_C = 19.5 G) in the α-position to the radical center. This indicates that the unpaired electron density on the central carbon atom of the spin-adduct of α-triketone is lower due to the delocalization on two oxygen atoms of the α-carbonyl groups.

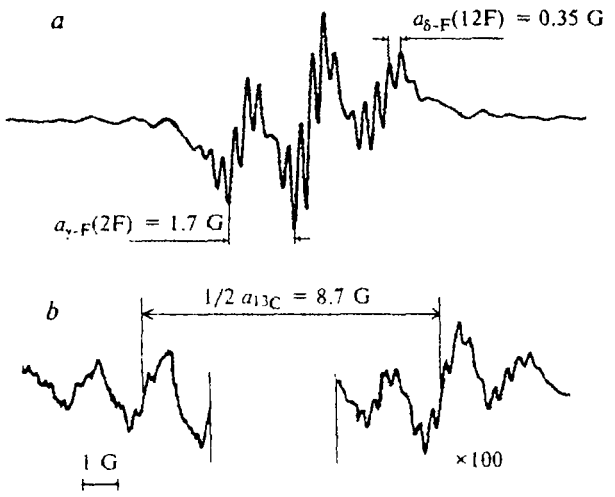
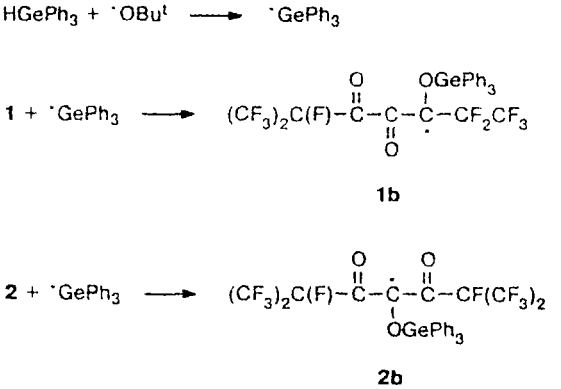


Fig. 2. ESR spectrum of radical **2a** at 300 K (*a*) and the low-field component of HFC with ^{13}C in radical **2a** (*b*).

Thus, the formation of adducts of types **1a** and **2a** is determined by both steric and electronic factors. The structure with the maximum delocalization of the unpaired electron is realized.

When the UV irradiation is stopped, the times of disappearance of spin-adducts **1a** and **2a** differ sharply: 12 s for **1a** at 300 K and 15 min for **2a**, and the intensity of the signal decreases not to zero, but to some stationary temperature-dependent level. Therefore, it can be assumed that the reverse dimerization is the main route of decay of spin-adducts **1a** and **2a**. Using the temperature dependence of the intensity of the signals, we estimated the enthalpy of the radical $\rightleftharpoons$ dimer equilibrium to be ≤ 2.7 kcal mol^{-1}.

The reaction of the Ge-centered radicals with α-triketones occurs *via* the scheme:



The direction of the reaction depends on the structure of α-triketone. In the case of **1**, the addition occurs at the oxygen atom of the carbonyl group directly bound to the ethyl group, $a_{\beta\text{-}F}(2F)$ = 11 G, $a_{\gamma\text{-}F}(4F)$ = 1 G.

In the case of symmetrical triketone **2**, the adduct of the addition at the central carbonyl group is identified, $a_{\gamma\text{-}F}(2F)$ = 2.1 G. There is a specific feature of the ESR spectrum of the spin-adduct of the Ge-centered radical with triketone **2** (Fig. 3, *a*, *b*): broadening of the central component of the triplet as the temperature decreases, and at 210 K, the γ-fluorine atoms of two perfluoroisopropyl groups become magnetically nonequivalent ($a_{\gamma\text{-}F}$ (1F) = 3.5 G, $a_{\gamma\text{-}F}$(1F) = 1.9 G) (*cf.* Ref. 3). This is related to the fact that the rotation of the bulky $Ge(C_6F_5)_3$ group becomes hindered, which affects the rotation of the perfluoroisopropyl groups. A similar situation was observed for the spin-adduct of the benzyl radical with triketone **2**. At 340 K, the ESR spectrum

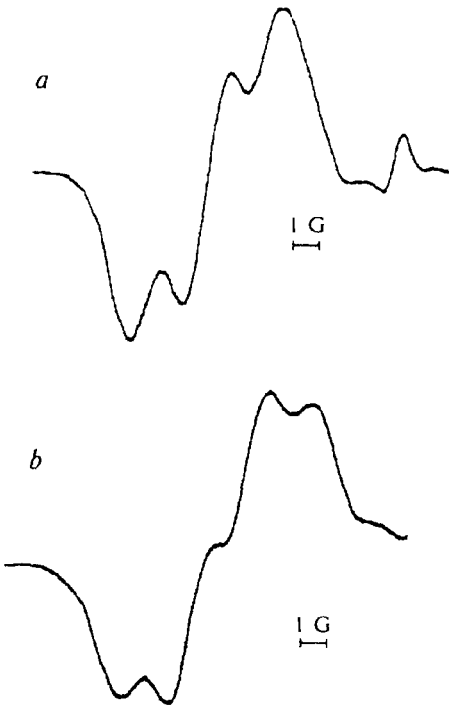


Fig. 3. ESR spectra of the spin-adduct of the Ge-centered radical with triketone **2** at 300 K (*a*) and 210 K (*b*).

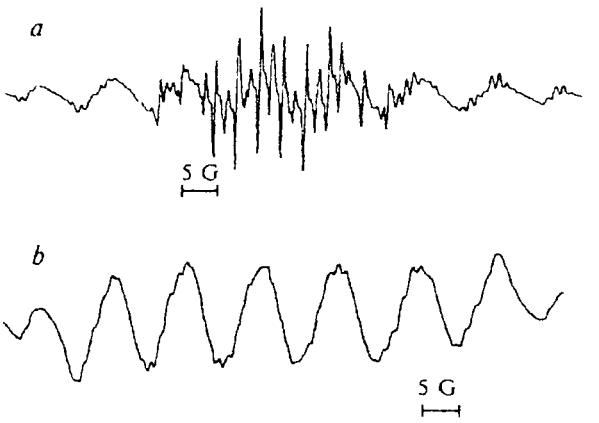


Fig. 4. ESR spectra of the spin-adduct of $^{\cdot}Mn(CO)_5$ and triketone **1** (*a*), as well as paramagnetic complex **1d** (*b*).

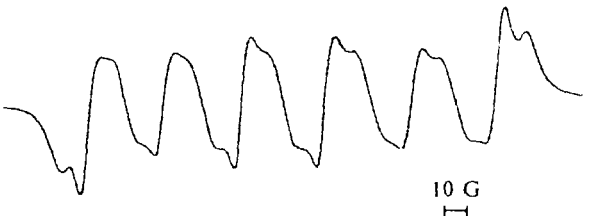
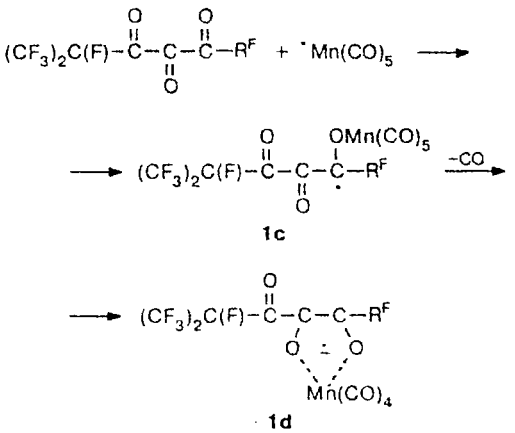


Fig. 5. ESR spectrum of paramagnetic complex **1e**.

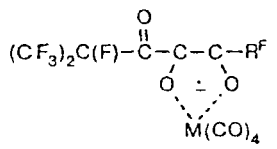
exhibits a triplet ($a_{\gamma\text{-}F}(2F)$ = 2.5 G), and when the temperature decreases to 240 K, a doublet of doublets is observed ($a_{\gamma\text{-}F}(1F)$ = 3.25 G, $a_{\gamma\text{-}F}(1F)$ = 1.5 G).

The study of the interaction of the metal-centered radicals $^{\cdot}M(CO)_5$ (M = Mn, Re) obtained from the corresponding dimers shows that at 220 K the Mn-centered radical is added to **1** at the oxygen atom of the carbonyl group adjacent to the ethyl group, $a_{\beta\text{-}F}(2F)$ = 7.25 G, a_{Mn} = 3 G (Fig. 4, *a*). It can be assumed that this is explained by the donor properties of the Ge- and Mn-centered radicals adding to a more electron-withdrawing (as compared to the central group) and less hindered carbonyl group.



When the temperature increases to 280 K, the spin-adduct is transformed into a paramagnetic complex ($a_{\beta\text{-}F}(2F)$ = 8.7 G, a_{Mn} = 9.5 G) (Fig. 4, *b*) by the intramolecular oxidation reaction.[4,5]

Similar results were obtained by the reactions of the Mn-centered radicals with **2**. For example, the ESR spectrum of the $^{\cdot}Mn(CO)_5$ spin-adduct at 220 K is a poorly resolved doublet ($a_{\beta\text{-}F}(1F)$ = 7.25 G), which is transformed upon heating to 280 K into a sextet with the HFC constant of the unpaired electron with the nucleus of the manganese atom of 9.5 G, which is characteristic of the final paramagnetic complex **2d** (M = Mn).



2d, e

R^F = C_2F_5, *i*-C_3F_7;
M = Mn (**d**), Re (**e**)

In the case of the addition of $^{\cdot}Re(CO)_5$ to **1** and **2**, the final paramagnetic complex **1e** (M = Re) or **2e** is immediately detected (a_{Re} = 37.5 G, a_F ~10 G) (Fig. 5).

Thus, the addition of the Si-centered radicals to α-triketones results in the formation of the radicals with the highest delocalization of the unpaired electron. These radicals form dimers with a low value of the enthalpy of the radical—dimer equilibrium. The germanium- and manganese-centered radicals characterized by stronger electron-donating properties are added to the oxygen atom of the carbonyl group bound directly to the

perfluoroethyl substituent, which is a more electron-withdrawing, as compared to the central group, and less hindered group.

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