

# ESR study of radicals formed by the reduction of $\alpha$ -diketones $C(O)C(O)CF_3$ ( $R = (CF_3)_2CF, C_6F_5, (CF_3)_3C$ ) with several Group I–III metals

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The ESR spectra of radical anions formed by reduction of  $\alpha$ -diketones  $RC(O)C(O)CF_3$  ( $R = (CF_3)_2CF, C_6F_5, (CF_3)_3C$ ) with metals (Li, Na, K, Mg, Cd, Zn, Hg, In, and Tl) in THF were studied. For  $R = (CF_3)_2CF$  and  $C_6F_5$ , the radical anions are formed as *cis*-isomers, whereas for  $R = (CF_3)_3C$ , *trans*-isomers are obtained. Line broadening due to solvation and desolvation of the cation is observed in the latter case. The reduction of  $\alpha$ -diketone  $(CF_3)_2CFC(O)C(O)CF_3$  with Group II metals (Mg, Cd, Zn) results in the formation of radical pairs.

**Key words:** ESR, radical anion, reduction,  $\alpha$ -diketone, radical pairs, fluorine.

Depending on various factors (the structure of substituents, the nature of counterion or solvent), semidiones, products of one-electron reduction of symmetric  $RC(O)C(O)R$  ( $R = Me, Et, Pr^a, Bu^i, Pr^i$ ) or asymmetric  $RC(O)C(O)Me$  ( $R = Et, Pr^a, Bu^i, Pr^i, Bu^i$ ) dialkyl-1,2-diketones, can be formed in *cis*- or in *trans*-forms that in some cases can be in chemical equilibrium.<sup>1</sup> The hyperfine coupling (HFC) of the unpaired electron with the nuclei of cations is observed in the ESR spectra of radical anions (RA) in the *cis*-form.<sup>1–3</sup> Additionally, the constants of HFC with the nuclei of  $\beta$ -hydrogen atoms in the *cis*-conformation are larger than those in the *trans*-conformation.<sup>1</sup> Similar peculiarities of ESR spectra were observed<sup>2</sup> in the reduction of perfluorodiacetyl [ $CF_3C(O)C(O)CF_3$ ]. However, the problem of the spin density distribution in *cis*- or *trans*-isomers was not considered in these works.

In this work, we investigated the ESR spectra of radical anions obtained by the reduction of  $\alpha$ -diketones  $RC(O)C(O)CF_3$  ( $R = (CF_3)_2CF$  (1),  $C_6F_5$  (2),  $(CF_3)_3C$  (3)) with Group I–III metals in order to study the effect of substituents and the cation nature on the structure and the spin density distribution.

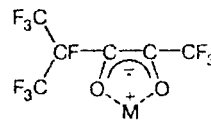
## Experimental

ESR spectra were recorded on a Varian E-12A spectrometer in degassed quartz ampules. The samples were irradiated by the focussed light of a DRSh-1000 lamp and thermostatted using a Unipan electronic temperature controller.  $\alpha$ -Diketones were reduced either with mercury amalgams of Li, Na, K, Zn, Mg, Cd, In, and Tl or by phototransfer of electron from  $MI_n$ .

$M = Na, K, Cd$  ( $n = 1, 2$ ) following the known procedure<sup>3</sup> in THF purified according to Ref. 4.

## Results and Discussion

Reduction of 1 with mercury amalgams and iodides of alkali metals for ~30 s results in the formation of primary RA whose ESR spectra (Table 1) are characterized by the interaction of the unpaired electron with the nuclei of  $\beta$ -fluorine atoms of the  $CF_3$  group, one  $\beta$ -fluorine atom, and six  $\gamma$ -fluorine atoms of the perfluoroisopropyl group with the nuclei of magnetic isotopes of metal cations. Hence it follows that all radical anions studied are in *cis*-form.



**Table 1.** HFC constants (G) of radical anions,  $(CF_3)_2CFC(O)C(O)CF_3$  derivatives

Reducing agent	$a_{\beta-F}(CF_3)$	$a_{\beta-F}(1 F)$	$a_{\gamma-F}(2 CF_3)$	$a_M$
NaI	12.5	4	1.75	0.5
Na/Hg	12.75	4	1.5	0.5
Li/Hg	12.5	4	1.5	0.875
Mg/Hg	11.5	1.75	1.75	—
Zn/Hg	10.5	1.25	3	—
Cd/Hg	11.25	1.5	3.1	10
CdI <sub>2</sub>	11.25	1.5	3.5	10
Hg	11.9	1.25	3.1	—
TlCp	12	1.75	3.5	52.25

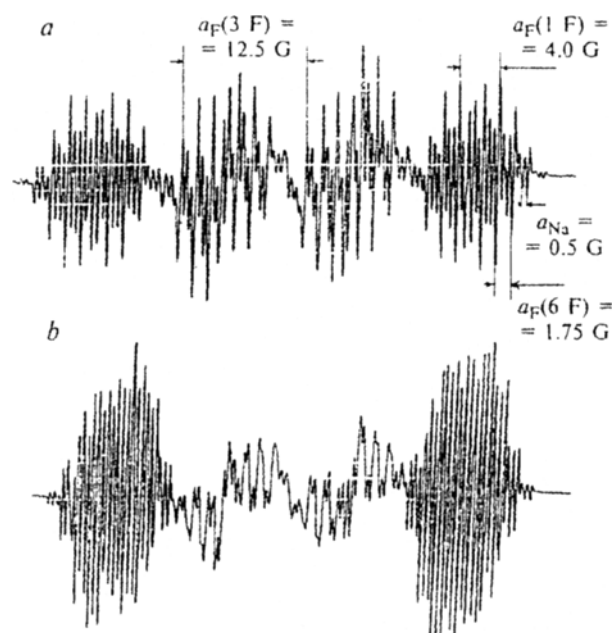
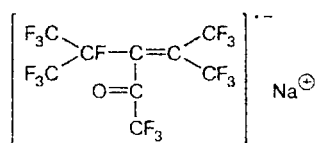


Fig. 1. ESR spectra of radical anions, products of the reduction of  $\alpha$ -diketone **1** by phototransfer of electron from NaI in THF, at 300 (a) and at 270 K (b).

The smaller values of the constants of HFC with the nucleus of the fluorine atom of the perfluoroisopropyl group compared with those of the  $\text{CF}_3$  group indicate that the  $(\text{CF}_3)_2\text{CF}$  group occupies such a fixed (in the ESR time scale) position with respect to the  $2p_z$ -orbital of the unpaired electron at which the  $\beta$ -fluorine atom lies near the nodal plane passing perpendicular to the  $2p_z$ -orbital axis (*cf.* Ref. 5). The ESR spectral pattern of radical anions with alkali metal cations changes appreciably and the central components of the quadruplet are broadened as temperature decreases. This is particularly noticeable in the ESR spectra of RA with  $\text{Na}^+$  cations (Fig. 1, a, b). Such a behavior of the spectral lines indicates hindered rotation of the  $\text{CF}_3$  group since in this case the sum of the constants of HFC changes slightly and the outer lines, in contrast to the central lines, are not broadened and their intensities remain unchanged.<sup>6</sup>

We observed analogous broadening of two central multiplets of the quadruplet associated with hindered rotation of the  $\text{CF}_3$  group in the reduction of the branched vinyl ketone with alkali metals ( $a_F(\text{CF}_3) = 37.5$  G).



The increase in the duration of the reduction with alkali metal amalgams to 5 min results in defluorination

Table 2. HFC constants (G) of radical anions —  $\text{C}_6\text{F}_5\text{C}(\text{O})\text{C}(\text{O})\text{CF}_3$  derivatives

Reducing agent	$a_{\beta\text{-F}}(\text{CF}_3)$	$a(o\text{-F})$	$a_M$
Na/Hg	12.75	4.0	0.75
Na/Hg+tetrahydrobenzo-18-crown-6	12.5	—	—
Mg/Hg	10	4	—
Zn/Hg	9.75	3.75	—
Cd/Hg	10.75	3.75	5.25
Tl/Hg	11.5	3.0	46.75

of initial RA with the formation of secondary radical products. No HFC with the nucleus of  $\beta$ -fluorine atom of the perfluoroisopropyl group is observed in their ESR spectra (**1a**,  $a_F(3\text{ F}) = 24.12$  G,  $a_F(6\text{ F}) = 0.5$  G; **1b**,  $a_F(3\text{ F}) = 14.25$  G,  $a_F(6\text{ F}) = 0.5$  G).

Radical anions of *cis*-structure are formed in the reduction of  $\alpha$ -diketone **2** with Na and Li amalgams, which is evidenced by the interaction of the unpaired electron with the nuclei of alkali metal atoms (Table 2). This reaction is accompanied by replacement of the fluorine atom in the *para*-position by the hydroxyl ion (*cf.* Ref. 7), so that the secondary product is already detected since no interaction of the unpaired electron with the nucleus of the  $\text{F}_{para}$  atom is revealed.

Reduction of  $\alpha$ -diketone **3** with Na and Li amalgams results in the formation of RA in the *trans*-form since no interaction of the unpaired electron with the nuclei of metal atoms is observed in the ESR spectra (Table 3).

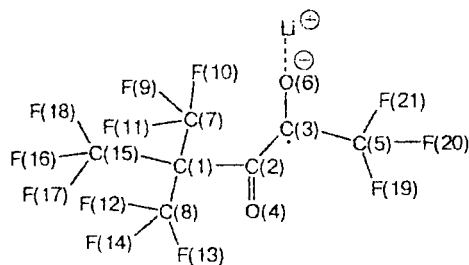


Table 3. HFC constants (G) of radical anions,  $(\text{CF}_3)_3\text{CC}(\text{O})\text{C}(\text{O})\text{CF}_3$  derivatives

Reducing agent	$a_{\beta\text{-F}}(\text{CF}_3)$	$a_{\gamma\text{-F}}(2\text{ CF}_3)$	$a_M$
NaI	9	0.5	—
Na/Hg	9	0.5	—
Na/Hg+tetrahydrobenzo-18-crown-6	8.6	0.5	—
Mg/Hg	12	1.5	—
Cd/Hg	8.38	1.95	—
Zn/Hg	9.2	1.7	—
Tl/Hg	9	1.7	19.5

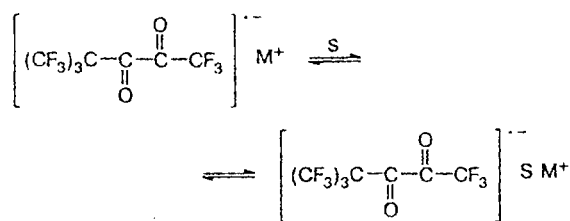
**Table 4.** The density of unpaired electron ( $\rho$ ) and the charge density ( $q$ ) in the *trans*-radical anion **3** and the C—O bond orders calculated by the MNDO method in the UHF approximation.

Ionic pair	$\rho/\text{au}$				$q/\text{au}$				Bond order/Å	
	C(2)	C(3)	O(4)	O(6)	C(2)	C(3)	O(4)	O(6)	C(2)—O(4)	C(3)—O(6)
SIP*	0.21	0.01	0.49	0.30	-0.08	0.17	-0.36	-0.34	1.485	1.711
CIP**	-0.09	0.45	0.33	0.32	0.16	-0.01	-0.25	-0.41	1.771	1.369

\* Solvent-separated ion pair. \*\* Contact ion pair.

To interpret the experimental data obtained, quantum-chemical calculations of radical anion **3** and its complex with lithium cation simulating the solvent-separated ionic pair (SIP) and the contact ionic pair (CIP), respectively, were performed by the MNDO method<sup>8</sup> in the UHF approximation with full geometry optimization. According to calculations, the *trans*-isomer is more thermodynamically stable in both cases. The density of the unpaired electron is asymmetrically distributed over the C(2), C(3), O(4), and O(6) atoms, especially in the case of non-solvated metal cation (Table 4). Thus, the RA obtained have the structure of "keto ketyl" (the species in which the spin density is localized mostly on one carbonyl group) rather than that of "semidiones" (species with symmetric spin and charge density distribution over two carbonyl groups).

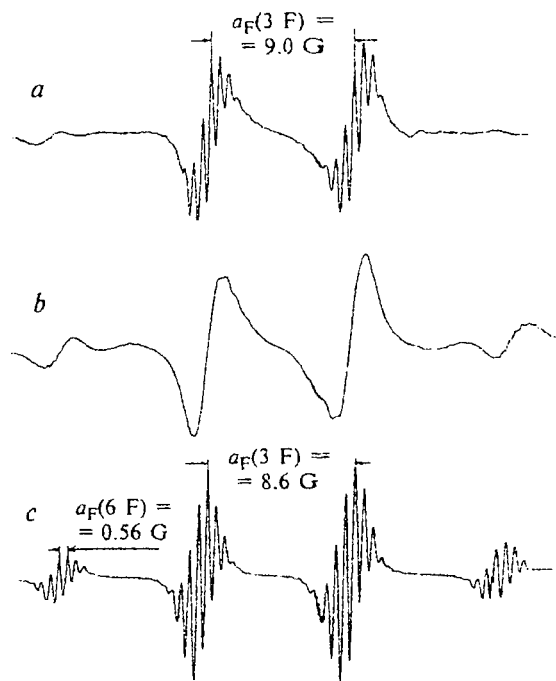
Broadening of the outer components of the quadruplet, which occurs as temperature increases from 190 to 300 K (Fig. 2, *a, b*) and is likely due to fast solvation and desolvation of the cation, is a peculiarity of the spectral behavior of RA **3** obtained by the reduction with alkali metals in THF. As can be seen from the data in Table 4, the unpaired electron density on the C(3) atom adjacent to the CF<sub>3</sub> group for the CIP and SIP differ substantially; at the same time, the constants of HFC with the nuclei of  $\beta$ -fluorine atoms and the unpaired electron density change in parallel. Hence it follows that the constants of HFC with the nuclei of fluorine atoms of the CF<sub>3</sub> group in the solvated and desolvated forms should be different, and therefore the fast exchange will result in the alternation of linewidths.



In fact, in the case of RA obtained by the reduction with sodium, the addition of tetrahydrobenzo-18-crown-6 to THF shifts the equilibrium towards the solvated cation. This results in a drastic change in the spectral pattern, and at 300 K the ratio of line intensities in the quadruplet becomes close to the binomial one (see Fig. 2, *c*). Based on the analysis of the line broadening

in ESR spectra of RA **3**, we evaluated the activation energy of cation solvation, which appeared to be close to 1 kcal mol<sup>-1</sup>.

Biradical paramagnetic complexes can be formed in the reduction of **1** with Group II—III metals. However, the photochemical reaction of **1** with CdI<sub>2</sub> and the reduction of **1** with Group III metals (In, Tl) results only in the formation of mono-RA in the *cis*-conformation (Fig. 3, *a, b*). No alternation of linewidths is observed for these RA as temperature decreases to 220 K, hence the rotation of CF<sub>3</sub> group remains free. Well-resolved signals of mono-RA in which the M<sup>2+</sup> cation is a counterion (the second anion might be the dianion or OH<sup>-</sup>) and a signal of the RA dimer broadened due to the dipole-dipole interaction are observed in the ESR spectra of products of the reduction of **1** with Mg, Zn, and Cd amalgams at room temperature (see Table 1). Freezing of the solutions down to 77 K makes it pos-

**Fig. 2.** ESR spectra of radical anions, products of the reduction of  $\alpha$ -diketone **3** with Na amalgam in THF: with no additives at 280 (*a*) and at 190 K (*b*); and with addition of tetrahydrobenzo-18-crown-6 at 280 K (*c*).

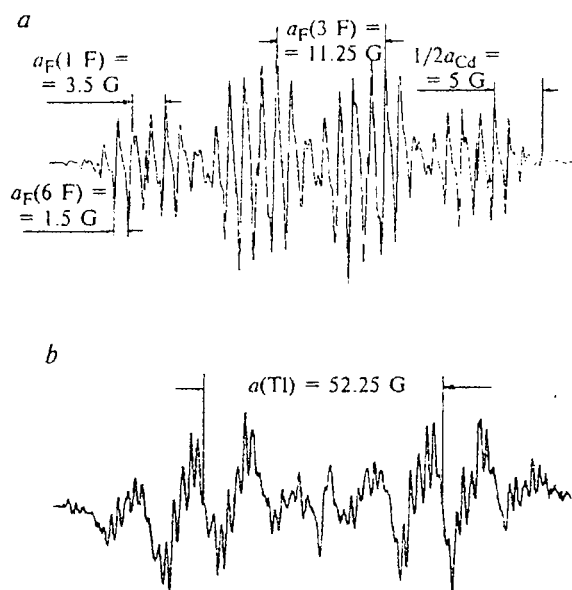


Fig. 3. ESR spectra of radical anions, products of the reduction of  $\alpha$ -diketone **1**: *a*, by phototransfer of electron from  $\text{CdI}_2$ ; *b*, with Tl amalgam.

sible to record characteristic spectra of radical pairs and to measure the magnitude of the spin-spin interaction  $D$  (Table 5).

Since the value of the parameter  $E$  characterizing the deviation of the spin density distribution from axial symmetry is equal to zero for all biradical complexes, one can conclude that the chelate sites of these complexes are tetrahedra with oxygen atoms of the ligands at the vertices (*cf.* Ref. 9).

We failed to record the spectra of radical pairs at 77 K in the case of reduction of **2** and **3** under analogous conditions.

The substantial decrease in the constant of HFC with the nucleus of thallium atom ( $a_{\text{Tl}} = 19.5$  G) as compared to the RA in the *cis*-conformation ( $a_{\text{Tl}} = 52.25$  G) is evidence for the *trans*-structure of mono-RA **3**.

Thus, the ESR spectra of RA formed by the reduction of **1**–**3** with metals (Li, Na, K, Mg, Cd, Zn, Hg, In, and Tl) in THF were studied. In the case of **1** and **2**,

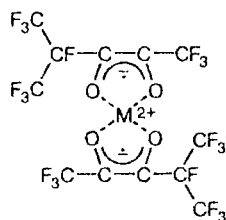


Table 5. Parameters of radical pairs ( $D/E$ ) (derivatives of **1**) in the zero magnetic field, the average distances between the radical centers ( $L$ ) in symmetric biradical complexes with Group II metals, and the ionic radii of elements ( $r$ )

$M^{2+}$	$(D/E)^*$	$L/\text{\AA}$	$r/\text{\AA}$
Mg	196/0	5.2	0.65
Zn	176/0	5.4	0.74
Cd	175/0	5.4	0.97

\*  $D$  and  $E$  values are given in G.

the radical anions obtained have the *cis*-conformation, whereas the derivatives **3** have the *trans*-conformation. Reduction of **1** with Group II metals (Mg, Cd, Zn) results in the formation of biradical paramagnetic complexes in which the chelate site is a tetrahedron with the oxygen atoms of  $\alpha$ -diketone at the vertices and the cation at the center.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32933).

## References

1. G. A. Russell, D. F. Lawson, H. L. Malkus, R. D. Stephens, G. R. Underwood, T. Takano, and V. Malatesta, *J. Am. Chem. Soc.*, 1974, **96**, 5830.
2. G. A. Russell, J. L. Gerlock, and D. F. Lawson, *J. Am. Chem. Soc.*, 1971, **93**, 4088.
3. G. A. Russell and J. L. Gerlock, *J. Am. Chem. Soc.*, 1974, **96**, 5838.
4. A. J. Gordon and R. A. Ford, *The Chemist's Companion*, J. Wiley and Sons, New York–London, 1972.
5. B. L. Tumanskii, T. V. Timofeeva, A. A. Kadyrov, N. N. Bubnov, S. P. Solodovnikov, K. N. Makarov, Yu. T. Struchkov, and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, 1990, **312**, 1152 [*Dokl. Chem.*, 1990 (Engl. Transl.)].
6. B. L. Tumanskii, N. N. Bubnov, V. R. Polishchuk, and S. P. Solodovnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2222 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].
7. S. V. Kulkarni and C. Trapp, *J. Am. Chem. Soc.*, 1970, **92**, 4809.
8. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
9. A. I. Prokof'ev, N. A. Malysheva, N. N. Bubnov, S. P. Solodovnikov, and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, 1980, **252**, 370 [*Dokl. Chem.*, 1980 (Engl. Transl.)].

Received March 24, 1998