ESR study of reversible complex formation between bis(η^5-cyclopentadienyl)vanadium and fullerene C_{60} in solution

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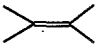
Using the ESR method, equilibrium complex formation of fullerene C_{60} with bis(η^5-cyclopentadienyl)vanadium in solutions in aromatic solvents was found to occur. Based on an analysis of isotropic (g_i = 2.0008; $A_i(V^{51})$ = −45.7 mT) and anisotropic (g_i = 1.9808; g_2 = 2.0135; $\langle g_3 \rangle$ = 2.0060; $A_1(^{51}V)$ = −7.85 mT; $A_2(^{51}V)$ = −6.50 mT; $\langle A_3(^{51}V) \rangle$ = 0.61 mT) ESR spectra parameters, it was established that the complex formed, $Cp_2V(\eta^2\text{-}C_{60})$, corresponds to vanadocene d^1-complexes with η^2-bonded ligands.

Key words: fullerene, ESR spectra, d^1-complexes of vanadocene.

The occurrence of oxidative addition reactions giving paramagnetic d^1-complexes is a characteristic feature of vanadocene chemistry.[1] The stability of its complexes with two-electron η^1- and η^2-ligands such as CO, CNR, alkynes, alkenes, *etc.* is determined by the electronic and steric properties of the neutral ligands. For example, although vanadocene does not form complexes with simple alkenes under ordinary conditions, it forms stable d^1-complexes with alkenes containing electron-withdrawing groups such as C(O)OR or CF_3.[2] The geometric structures of coordinated alkenes in such complexes, which are of the metallocycle type, are distorted substantially. According to data in Ref. 2, the length of the C=C double bond in the vanadocene—diethyl fumarate adduct is increased to 1.468 Å, while the dihedral angle between the planes passing through the double bond and the pair of bonds, which connect the corner atoms at the double bond with the substituents, equals 129.7°.

An analysis of the molecular parameters of fullerene C_{60} shows that the geometry of the  fragments, which constitute the frame of the molecule, is similar to that of coordinated alkenes involved in metallocycles in vanadocene complexes.[2] The mean C=C bond length is 1.398(10) Å according to gas-phase electron diffraction data[3] and 1.399(7) Å according to data of X-ray diffraction at 110 K,[4] while the dihedral angle between the planes that pass through the double bond and the two single bonds is 138.6°. Thus, the structural parameters of C_{60} render it suitable for complexing with the coordination-unsaturated vanadocene molecule, and complexing between them can be expected with high probability.

In the present work, the interaction of vanadocene with C_{60} was studied by an ESR technique. When equimolar amounts of $3 \cdot 10^{-3}$ mol L^{-1} solutions of C_{60} and vanadocene in toluene are mixed at room temperature (290 K), no visible changes occur. The color of the solution determined by the intense absorption band of C_{60} (λ = 560 nm) remains almost unchanged. However, a low-intensity octet with anisotropically broadened components (Fig. 1, *a*) typical of paramagnetic vanadium derivatives (^{51}V; 99.76 %; I = 7/2; μ_N = 5.1392) appears in the ESR spectrum.

Cooling the solution to 240 K (Fig. 1, *b*) results in a ~40-fold growth in the intensity of the ESR signal observed. Simultaneously, the color of the solution changes from reddish-violet through yellowish-green to black-green. When the solution is heated to the original temperature (290 K), the original color and intensity of the ESR signal are restored.

The changes observed indicate equilibrium complexing between C_{60} and vanadocene (Eq. 1) in solution.

$$Cp_2V + C_{60} \rightleftharpoons Cp_2V(\eta^2\text{-}C_{60}) \qquad (1)$$

The equilibrium is shifted almost completely to the right at low temperatures close to the melting point of toluene (178 K). This conclusion follows from an analysis of the anisotropic ESR spectrum, which reflects the equilibrium state at this temperature. The spectrum does not display absorption typical of the starting Cp_2V in a magnetic field of about g = 4, which indicates it is completely bound in the complex. In a magnetic field of g = 2, the ESR spectrum (Fig. 2) is typical of anisotropic spectra of vanadocene d^1-complexes.[1] An analysis of the parameters of the isotropic (g_i = 2.0001; $A_i(V^{51})$ = −4.58 mT) and anisotropic (g_1 = 1.9808; g_2 = 2.0135; $\langle g_3 \rangle$ = 2.0060; $A_1(^{51}V)$ = −7.85 mT; $A_2(^{51}V)$ =

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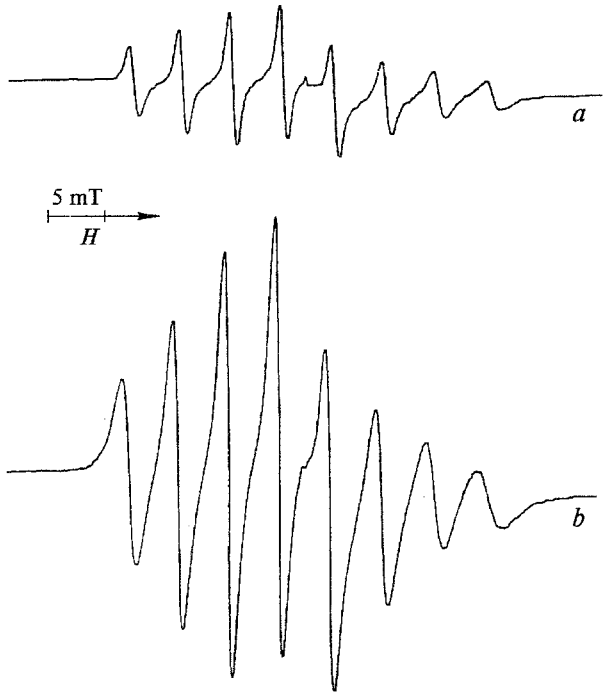

Fig. 1. Isotropic ESR spectrum of the $Cp_2V(\eta^2\text{-}C_{60})$ complex in toluene: *a*, at 280 K; *b*, at 240 K.

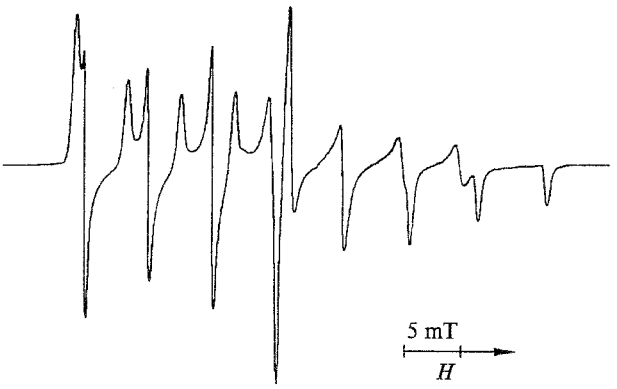

Fig. 2. Anisotropic ESR spectrum of the $Cp_2V(\eta^2\text{-}C_{60})$ complex in toluene at 150 K.

-6.50 mT; $\langle A_3(^{51}V)\rangle = 0.61$ mT) ESR spectra and their comparison with those of known paramagnetic vanadocene complexes[1] suggests that the complex studied belongs to the class of vanadocene d^1-complexes with η^2-bound ligands. In this complex, C_{60} is bound to the vanadium atom *via* the two carbon atoms linked by a double bond; this gives a three-membered metallocycle, $Cp_2V(\eta^2\text{-}C_{60})$, in analogy to known complexes of vanadocene with alkenes[1,2] and alkynes.[1,5]

When the concentration of the starting reagents is increased or the reaction mixture is kept for several hours at 200—220 K, a fine-crystalline black powder precipitates from the solution. According to elemental analysis data, the product formed corresponds to the $Cp_2V(\eta^2\text{-}C_{60})$ complex. Dissolution of this product in toluene results in solutions whose properties are identical (ESR and electron absorption spectra) to those obtained by dissolving equimolar amounts of Cp_2V and C_{60}.

A preliminary ESR study shows that C_{60} can add at least two more moles of Cp_2V in a similar way to give complexes with a higher content of Cp_2V groups, in which C_{60} acts as a polyfunctional ligand, like in its known complexes with $Pt(PMe_3)_2$.[6]

The $Cp_2V(\eta^2\text{-}C_{60})$ complex studied in this work is the first example of metallocene derivatives of C_{60} in which a metal atom is directly bonded to C_{60}. Taking into consideration the similarity of the chemistry of titanocene, niobocene, and molybdenocene to that of vanadocene, we can expect that these metallocenes should also form complexes having similar structures.

At present, such complexes are being synthesized; an X-ray diffraction study of the molecular structure of the $Cp_2V(\eta^2\text{-}C_{60})$ complex is in progress, and its physical and chemical properties are being studied.

Experimental

C_{60} was obtained and purified by a procedure reported previously;[7] bis(cyclopentadienyl)vanadium was synthesized by a known procedure.[8] ESR spectra were recorded on a Bruker ER 200D SRC spectrometer with a standard (ER 4102 ST) or double (ER 4105 DR) resonator at a working frequency of 9.34 MHz. The samples were thermostatted using an ER 4111 VT temperature controlling device. The *g*-factor was determined using the DFPH standard. The parameters of the ESR spectra were calculated taking into account corrections obtained by the Breit—Rabi equation.[9] The values of g_3 and $A_3(^{51}V)$ were calculated using the equations $g_i = 1/3 \cdot (g_1 + g_2 + g_3)$, $A_i(^{51}V) = [A_1(^{51}V) + A_2(^{51}V) + A_3(^{51}V)]$.

Reaction of C_{60} with Cp_2V. An evacuated ampoule containing C_{60} (0.110 g, 0.152 mmol) in toluene (40 mL) was charged with a solution of Cp_2V (0.083 g, 0.458 mmol) in toluene (15 mL) with stirring. After cooling to $-10 \div -15$ °C, a black fine-crystalline powder precipitated from the dark-brown solution. The powder was separated by centrifuging and washed with hexane (1×15 mL) to give 0.053 g of a black powder of the composition Cp_2VC_{60}. Found (%): C, 92.82; H, 0.73; V, 4.74. $C_{70}H_{10}V$. Calculated (%): C, 93.34; H, 1.11; V, 5.55. The solvent was removed by condensing *in vacuo*, and the residue was washed with hexane (3×25 mL) to give 0.112 g of a dark brown powder. IR (oil, ν/cm^{-1}): 525 m, 575 m (C_{60}); 720 s, 800 s, 950 m, 1020 m (Cp).

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