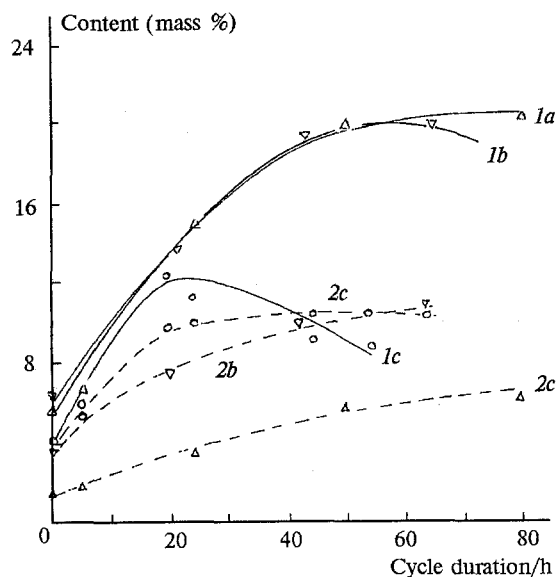


Table 1. Degree of conversion of CO₂ and composition of the reaction products (the duration of circulation is 40 h)

T/K	Degree of CO ₂ conversion	Composition of reaction products		
		CO	CH ₄	C ₂ –C ₄
293	1.2	1.0	0.2	—
373	2.0	1.5	0.2	0.3
593	11.5	7.8	1.8	1.9
623	28.4	20.0	6.0	2.4

**Fig. 1.** Dependence of the proportion of CO (1) and C₁–C₄ hydrocarbons (2) in the gaseous products on the duration of the cycles with one batch of intermetallide: first (a), second (b), and third (c) cycles ($T = 623$ K, $p = 8$ atm).

(11–28 % (w/w)) occurs at 593–623 K. In this temperature range, decomposition of the hydride phase of intermetallide and desorption of hydrogen occur.

In the first cycle, CO₂ is mostly converted into CO (80 %) (Fig. 1), and in the subsequent cycles, the proportion of C₁–C₄ hydrocarbons increases. This variation of the composition of the products may be associated with catalytic effect of iron, incorporated in the intermediate, on the synthesis of hydrocarbons from the CO, formed in the reaction, and the desorbed active hydrogen.

The results obtained indicate that the desorption of active hydrogen from the lattice of the iron-titanium intermetallide ensures a noticeable degree of conversion of CO₂ adsorbed on the surface, and this effect is observed even at room temperature. The latter allows iron-titanium alloys to be regarded as promising materials for developing active catalysts of the low-temperature conversion of CO₂.

References

1. E. V. Evdokimova, V. V. Lunin, P. V. Afanasiev, and I. I. Moiseev, *Mendeleev Commun.*, 1993, **1**, 1.
2. I. I. Moiseev, E. V. Evdokimova, V. V. Lunin, P. V. Afanasiev, A. E. Gekhman, and A. R. Gromov, *Dokl. Akad. Nauk*, 1993, **332**, 195 [*Dokl. Chem.*, 1993, **332** (Engl. Transl.)].
3. B. A. Kalachev, A. A. Il'in, V. A. Lavrenko, and Yu. V. Livinskii, *Gidridnye sistemy [Hydride Systems]*, Metallurgiya, Moscow, 1992, 350 pp. (in Russian).

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New complex of fullerene with an organic donor: (C₆₀)₂ · TPDP · (CS₂)

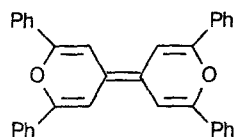
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The discovery of superconductivity characterized by high temperatures of the superconducting transition¹ in M₃C₆₀ salts (M is an alkali metal) and the discovery of ferromagnetic properties in TDAE · C₆₀ salts (see Ref. 2) have awakened considerable interest in studying compounds of C₆₀ with organic donors. The use of these

donors opens up broad possibilities for the synthesis of substances with various packings of C₆₀ in the crystal, which finally determines different properties of these compounds. At present, molecular complexes of fullerene with various donors including S- and Te-containing derivatives of tetrathiafulvalene have been prepared.^{3,4}

We synthesized the first charge transfer complex of C₆₀ with 2,2',6,6'-tetraphenyldipyranylidene (TPDP) as the donor, (C₆₀)₂ · TPDP · (CS₂)₄ (**1**).



1

This compound was obtained by evaporation (for 7 days at ambient temperature under argon) of a solution containing equimolar amounts of TPDP and C₆₀ in carbon disulfide, as well-formed black crystals looking as rhombs with a characteristic crater in the middle. Found (%): C, 86.20; H, 0.86; S, 10.88. C₁₅₈H₂₄O₂S₈. Calculated (%): C, 86.00; H, 1.08; S, 11.51.

The TG and DTG curves obtained in thermogravimetric analysis (20 to 700 °C, argon atmosphere) indicate that between 125 °C and 200 °C, this compound loses 12 % of its mass. This corresponds to the complete removal of CS₂ from the complex, which is confirmed by the absence of the band at 1508 cm⁻¹ from its IR spectrum. During further heating, in the 320–600 °C temperature range, the donor gradually decomposes; the loss of mass is 15 %. The IR spectrum of the residue (73 % of the total mass) exhibits absorption bands (AB) of the individual C₆₀ against the background of a broad band, probably associated with the carbon, resulting from decomposition of TPDP.

The IR spectra (Specord 75-IR, pellets with KBr) contain all the AB corresponding to the components of the complex. The bands at 1425, 1175, 575, and 525 cm⁻¹ are due to vibrational modes of C₆₀, their frequencies and the ratios between their intensities are unchanged with respect to individual C₆₀. The band at 1508 cm⁻¹ corresponds to ν(CS) in CS₂. TPDP is responsible for the AB at 3070, 3038, and 3015 cm⁻¹ (ν(CH)); 1655, 1592, and 1488 cm⁻¹ (ν(CC)); 1064 and 911 cm⁻¹ (in-plane δ(CCH)); and 755 and 685 cm⁻¹ (out-of-plane δ(CH)). As a result of complex formation,

the ν(CH) and δ(CCH) AB shift to the low-frequency region, the ν(CC) band is broadened, and the intensity of δ(CH) increases by a factor of 1.5.

The X-ray photoelectron spectrum exhibits no peak associated with the S atom, since CS₂ is removed from the complex during evacuation. The half-widths of C1s peaks exhibited by the complex (1.9 eV) and the initial C₆₀ (1.8 eV) are approximately identical, while that exhibited by the donor, TPDP, is somewhat higher (2.2 eV). The charge states of the carbon atoms of TPDP and C₆₀ incorporated in the complex are similar, possibly due to the exchange by π-electrons or due to the fact that fullerene makes the major contribution to the spectrum. The energy of the main plasmon for the complex (ħω_p = 25.5 eV) is lower than that for C₆₀ (26.1), which is apparently caused by interaction of TPDP (ħω_p = 21.3 eV) with C₆₀.

The electric conductivity of a single crystal of **1** is 10⁻⁷ (Ohm · cm)⁻¹, which is typical of weak charge-transfer complexes.

Thus, the (C₆₀)₂ · TPDP · (CS₂)₄ compound obtained by us is a molecular complex with weak charge transfer. It is probably formed through π-π interaction of the phenyl rings of TPDP with the π-system of fullerene.

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References

1. D. W. Murphy, M. J. Rosseinsky, R. M. Fleming, R. Tycko, A. P. Ramirez, R. C. Haddon, T. Siegrist, G. Dabbagh, J. C. Nully, and R. E. Walstedt, *J. Phys. Chem. Solids*, 1992, **53**, 1321.
2. P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holzer, S. Donovan, G. Gruner, and J. D. Thompson, *Science*, 1991, **253**, 301.
3. T. Pradeep, K. K. Singh, P. B. Sinha, and D. E. Morris, *J. Chem. Soc., Chem. Commun.*, 1992, 1747.
4. A. Izuoka, T. Tachikawa, T. Sugawara, T. Suzuki, and M. Konno, *J. Chem. Soc., Chem. Commun.*, 1992, 1472.

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