REACTION OF STYRENE WITH SULFUR AND TRIIRON DODECACARBONYL AND THE MOLECULAR STRUCTURE OF THE COMPLEX  $Fe_2(CO)_6(SCH_2S)$ 

A. I. Nekhaev, B. I. Kolobkov, M. T. Toshev, Kh. B. Dustov, and G. G. Aleksandrov UDC 542.91:548.737:547. 538.141:546.22:541. 49:546.725

Reaction of excess styrene with  $Fe_3(CO)_{12}$  and sulfur (60°C, 15 h, Ar, S/Fe<sub>3</sub>(CO)<sub>12</sub> 0.6 g-atom/mole) gave  $Fe_2(CO)_6S_2$ ,  $Fe_3(CO)_9S_2$ ,  $Fe_2(CO)_6(S_2CO)$ ,  $Fe_2(CO)_6S_2(PhCHCH_2)$ , PhCHCH<sub>2</sub>S<sub>4</sub>, and a novel binuclear complex  $Fe_2(CO)_6(S_2CH_2S)$ , whose structure was analyzed by x-ray crystallography. The crystals are monoclinic, a = 7.764(3), b = 13.205(4), c = 6.628(6) Å,  $\beta = 98.97(3)^\circ$ . V = 671.2(7) Å<sup>3</sup>, Z = 2, space group  $P2_1/m$ . The bond lengths are Fe-Fe 2.520(2), Fe-S 2.236(2), S-S 2.078(4), C-S 1.825(12), Fe-CO 1.784(8), and C=O 1.148(9) Å.

The reactions of sulfur and triiron dodecacarbonyl with linear [1, 2] and cyclic unsaturated hydrocarbons [3, 4] have been studied previously. These reactions have been shown [5] to proceed primarily via addition of two sulfur atoms to the double bond in the olefin, resulting in the formation of dithiodiiron hexacarbonyl complexes.

Our goal in the present paper was to examine the characteristics of this reaction in the case of a double bond in conjugation with an aromatic ring. Styrene was chosen as the unsaturated compound substrate.

## RESULTS AND DISCUSSION

Reaction of excess styrene with sulfur and  $Fe_3(CO)_{12}$  results in the formation of a mixture of sulfur-containing iron carbonyl complexes, a styrene complex (I), a polysulfide (II), and a novel binuclear complex (III), containing a bridging  $-S_2-CH_2-S-$  ligand.

$$\begin{aligned} PhCH = CH_2 + S_8 + Fe_3(CO)_{12} &\longrightarrow Fe_2(CO)_8S_2 + Fe_3(CO)_9S_2 + Fe_3(CO)_{10}S + \\ & S \xrightarrow{\qquad CH_2} \\ + Fe_2(CO)_8(S_2CO) + Fe_2(CO)_8S_2(PhCHCH_2) + PhCHCH_2S_4 + & S \xrightarrow{\qquad I \\ S \xrightarrow{\ I \\ S \xrightarrow{\qquad I \\ S \xrightarrow{$$

Iron carbonyls have been shown previously [6] to react with Lewis bases, including sulfur, for example, via radical intermediates. Complex (I) can be formed either from styrene and  $Fe_2(CO)_6S_2$  [7], or from polysulfide and an iron carbonyl. In reactions with polysulfide compounds iron carbonyl complexes always remove only two sulfur atoms from the polysulfide chain [3, 8]. Upon storage at ca. 20°C polysulfide (II) is converted gradually to a polymeric product. Reaction of (II) with  $Fe_3(CO)_{12}$  proceeds readily to give complex (I),  $Fe_2(CO)_6S_2$ , and  $Fe_3(CO)_9S_2$ .

Among the products of the reaction of styrene with sulfur and  $Fe_3(CO)_{12}$  the binuclear complex (III) stands out from the rest in terms of its unusual structure. The  $-CH_2$ - fragment in the (polysulfide) ligand in complex (III) may arise via insertion of a  $CH_2$  carbene species into an S-S bond of the polysulfide (II). Insertion of methylene fragments, formed via decomposition of diazomethane, into S-S [9] ane Te-Te [10] bonds in  $Fe_2(CO)_6E_2$  (E = S, Te) is known from the literature. In the example studied herein the  $CH_2$  fragment may arise via

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Technological Institute of Food and Light Industry, Bukhara. All-Union Scientific Reasearch Institute of Antibiotics, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 930-934, April, 1991. Original article submitted July 3, 1990.



Fig. 1. Overall molecular structures of (III) and its principal geometric parameters.

abstraction of H atoms from the hydrocarbon substrate by a carbon atom. The carbon atom source, in turn, may be the Bell-Buduar reaction, namely, disproportionation of carbon monoxide to give carbon dioxide and carbon. Considertion of the change in Gibbs free energy for the Bell-Buduar reaction as a function of the temperature reveals that the reaction is thermodynamically possible under standard conditions [11].

The unexpected or unusual structure of complex (III) was established based on the x-ray crystal structure analysis (cf. Experimental section), and is shown in Fig. 1.

Two  $Fe(CO)_3$  fragments are connected via an Fe-Fe bond and two S atoms in a bridging  $S_2CH_2S$  ligand. The crystallographic symmetry of the molecule is  $C_S$  (the mirror plane m passes through the nonhydrogen atoms in the bridging ligand perpendicular to the Fe-Fe bond).

The carbon atom in the  $S_2CH_2S$  ligand is connected to the two sulfur atoms by S-C bond lengths of 1.824(11) and 1.825(13) Å. The coordination around the Fe atoms is distorted octahedral, while the Fe<sub>2</sub>S<sub>2</sub> fragment adopts a "butterfly" conformation. The dihedral angle between the two FeFeS planes is 105.3°, which is substantially greater than the 90.4-91.0° dihedral angles found in complexes where two sulfur atoms are connected via a bridging carbon atom. The average Fe-CO and C $\equiv$ O bond lengths are 1.784 and 1.148 Å, respectively, and the Fe-C-O units are almost linear (178°).

The principal structural parameters in related diironhexacarbonyl complexes are summarized for comparison purposes in Table 1. The significant structural parameters changes observed in the compound  $Fe_2(CO)_6S_2CH_2$  [12] are associated with steric strain in the  $Fe_2S_2CH_2$ ring system. Thus, its SCS angle is only 94.55(3)°, while in (III) the related angle is 112.7(6)°. The remaining angles in the  $Fe_2S_3CH_2$  ring are as follows: FeFeS 55.9(1) and 55.6-(1), FeSS 106.3(1), FeSC 107.6(4), and SSC 100.7(4)°.

## EXPERIMENTAL

<sup>1</sup>H NMR spectra were recorded on a Varian T-60 (60MHz) spectrometer using TMS as internal standard. IR spectra were obtained on a UR-20 spectrophotometer. Mass spectra were measured on a Varian MAT-311A spectrometer using a system for direct sample introduction to the ion source, at an ionizing electron energy of 70 eV. The course of the reaction was followed by TLC using Silufol UV-254 plates with n-heptane as eluent. The reaction mixture was separated by adsorption column chromatography on a 1 m × 5 cm silica gel L (100-400  $\mu$ ) column (Chemapol, Czechoslovakia).

<u>Reaction of Styrene with Sulfur and  $Fe_3(CO)_{12}$ .</u> A mixture of 19.2 g (0.06 g-atom) sulfur, 50.4 g (0.1 mole)  $Fe_3(CO)_{12}$ , and 200 ml styrene was stirred for 15 h at 60°C under an argon

TABLE 1. Interatomic Bond Lengths (Å) and Angles (deg) in complexes  $Fe_2(CO)_6S_3CH_2$ ,  $Fe_2(CO)_6S_2CH_2$  [12],  $Fe_2(CO)_6(SCH_2)_2$  [13],  $Fe_2(CO)_6(SC_2H_4SO)$  [14], and  $Fe_2(CO)_6S_2$  [15]

Compound	Fe—Fe	Fe—S	s–s	FeSFe	SFeS
$Fe_{2}(CO) _{6}S_{3}CH_{2}$ $Fe_{2}(CO) _{6}S_{2}CH_{2}$ $Fe_{2}(CO) _{6}(SCH_{2})_{2}$ $Fe_{2}(CO) _{6}(SC_{2}H_{4}SO)$ $Fe_{2}(CO) _{6}S_{2}$	2,520 (2)	2,236 (2)	2,078(4)	68,6(1)	82,1(1)
	2,485 (1)	2,262 (1)	2,673(2)	66,64(4)	72,5(4)
	2,502 (1)	2,239 (1)	2,887(1)	67,96(3)	80,3(4)
	2,528 (1)	2,201 (1)	2,747(1)	70,19(3)	77,3(4)
	2,552 (2)	2,228 (2)	2,007(5)	69,9(1)	53,5(1)

TABLE 2. Atomic Coordinates (Fe, S  $\times 10^4$ , other  $\times 10^3$ ) in Complex (III)

Atom	x	y	Z
Fe	7410(1)	3454(1)	2952(1)
S(1)	8221 (3)	2500(0)	458(4)
S(2)	9378(4)	2500(0)	4894(4)
S (3)	11589(4)	2500 (0)	3486(5)
$\tilde{\mathbf{O}}(\mathbf{f})$	409(1)	390(1)	33(1)
O(2)	595(1)	407(1)	656(1)
O(3)	942(1)	529(1)	238(1)
C(1)	540(1)	374(1)	134(1)
$\mathbf{C}(2)$	650(1)	383(1)	515(1)
C(3)	862(1)	459(1)	262(1)
Č(4)	1060(2)	250 (0)	80 (2)

atmosphere (to complete disappearance of  $Fe_3(CO)_{12}$ , based on TLC). The complex  $Fe_3(CO)_{10}S$  is present in the reaction mixture only while  $Fe_3(CO)_{12}$  is still present [5]. The reaction mixture was cooled to ca. 20°C, filtered, and the precipitate was washed with hot (~50°C) benzene (1 liter). Styrene and benzene were removed on a rotary evaporator, and the residue was subjected to column chromatography on silica gel with petroleum ether (40-70°C) as eluent. Yield (in order of elution, %):  $Fe_2(CO)_6S_2$  (10),  $Fe_3(CO)_9S_2$  (8),  $Fe_2(CO)_6(S_2CO)$  (0.5), (III) (0.5), (II) (4), and (I) (10).

 $\frac{\text{Complex (I)}}{1957 (C\equiv 0)}, \text{ Dark red oil. IR spectrum (hexane, <math>v$ , cm<sup>-1</sup>): 2081, 2042, 2012, 1998, 1962, 1957 (C\equiv 0), 3090, 3070, 3035 (CH, CH<sub>2</sub>). 1600, 1585, 1495 (Ph). Mass spectrum, m/e: 448 (M<sup>+</sup>), 280 ([M - 6 CO]<sup>+</sup>), 176 ([Fe<sub>2</sub>S<sub>2</sub>]<sup>+</sup>), 104 ([PhCHCH<sub>2</sub>]<sup>+</sup>). <sup>1</sup>H NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 7.20 (5H, C<sub>6</sub>H<sub>5</sub>), 3.67 (1H, CH), 2.89 (1H, CH<sub>2</sub>), 2.21 (1H, CH<sub>2</sub>). Found: C 37.28; H 1.88; Fe 24.89; S 14.34%. C<sub>14</sub>H<sub>8</sub>FeS<sub>2</sub>O<sub>6</sub>. Calculated: C 37.53; H 1.80; Fe 24.93; S 14.31%.

<u>5-Phenyl-1,2,3,4-tetrathiacyclohexane (II)</u>. mp 36-37°C (hexane). Mass spectrum, m/e: 232 (M<sup>+</sup>), 104 ([M - 4S]<sup>+</sup>). Found: C 41.18; H 3.35; S 55.20%. C<sub>8</sub>H<sub>8</sub>S<sub>4</sub>. Calculated: C 41.34; H 3.47; S 55.19%.

<u>Complex (III)</u>. Mass spectrum, m/e: 390 (<sup>+</sup>), 222 ( $[M - 6 CO]^+$ ), 176 ( $[Fe_2S_2]^+$ ). Found: C 21.30; H 0.50; Fe 28.89; S 24.49%. C<sub>7</sub>H<sub>2</sub>Fe<sub>2</sub>O<sub>6</sub>S<sub>3</sub>. Calculated: C 21.56; H 0.52; Fe 28.64; S 24.67%.

<u>Reaction of Polysulfide (II) with  $Fe_3(CO)_{12}$ </u>. A mixture of 0.23 g (0.001 mole) (II) and 0.1 g (0.002 mole)  $Fe_3(CO)_{12}$  in 10 ml benzene was heated with stirring for 2.5 h at 60°C to complete disappearance of the polysulfide, based on TLC analysis. The reaction mixture was filtered, and the precipitate was washed with hot (50°C) benzene (10 ml). After solvent evaporation on a rotary evaporator the residue was subjected to column chromatography on silica gel [with petroleum ether (40-70°C) as eluent];  $Fe_2(CO)_6S_2$ ,  $Fe_3(CO)_9S_2$ , and complex (I) were isolated sequentially in quantitative yield.

<u>X-Ray Structure Analysis of Compound (III)</u>. The unit cell parameters and reflection intensities for a single crystal of (III) were measured using a Syntex Pl automated diffractometer ( $\lambda$  Mo K $\alpha$ , graphite monochromator,  $\theta/2\theta$  scanning in the range 2°  $\leq 2\theta \leq 55^{\circ}$ ). Crystals

of (III) are monoclinic: a = 7.764(3), b = 13.205(4), c = 6.628(6) Å,  $\beta$  = 98.97°, V = 671.2(7) Å<sup>3</sup>, Z = 2, P2<sub>1</sub>/m space group. The structure was solved using the heavy atom method and was refined by least squares using anisotropic approximations, to give R = 0.0556 and R<sub>w</sub> = 0.0551, based on 859 reflections with F<sup>2</sup>  $\geq$  2 $\sigma$ . The atomic coordinates are listed in Table 2.

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