Journal of Organometallic Chemistry, 149 (1978) 355—370

SYNTHESIS AND SOME PROPERTIES OF SULFUR-CONTAINING IRON TRICARBONYL COMPLEXES

N.S. NAMETKIN *, V.D. TYURIN and M.A. KUKINA

The A.V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow B-71, Leninskii prosp. 29 (U.S.S.R.) and the I.M. Gubkin Institute of Petrochemical and Gas Industry, Moscow (U.S.S.R.)

(Received October 26th, 1977)

Summary

Synthesis of $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$ by direct substitution of the carbonyl ligands in iron carbonyls with sulfur is described. The relative reactivities were determined for both iron carbonyls and organosulfur compounds in reactions of R_2S, R_2S_2 and RSH (R = alkyl, aryl) with $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. The properties of the $[RSFe(CO)_3]_2$ obtained are studied. New methods are found for their regeneration in the form of sulfides, disulfides and thiols.

Introduction

No information is available on reactions of sulfur with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. Sulfur does not substitute CO in $Fe(CO)_5$ at low temperature in CCl_4 and xylene solutions [1]. At the same time $Fe(CO)_5$ reacts vigorously with CCl_4, the carbonyl decomposing into iron chloride with simultaneous formation of hexachloroethane and phosgene [2].

The compounds of dithiodiironhexacarbonyl $S_2Fe_2(CO)_6$ (I) and dithiotriironnonacarbonyl $S_2Fe_3(CO)_9$ (II) have been synthesized indirectly from tetracarbonyl ferrate and sulfite or polysulfide ions [3], under drastic conditions from Fe, S and CO [4], from cyclohexene sulfide and 3-chloropropene sulfide [5], from 2-thiobenzthiazol [6], from different compounds with the C=S group [7—10] and from bis(thiocarbonyl)disulfane [11] as well as being obtained as the by-products in reactions of iron carbonyls with various organosulfur compounds. The highest yield of II was 55% [5].

It is known that thiols, disulfides and sulfides react with iron carbonyls to give the respective bis(alkyl- and aryl-thioirontricarbonyls) $[RSFe(CO)_3]_2$, R = alkyl, aryl (III) [12—18].

Reactions of the secondary and tertiary thiols, R = *iso*-C_3H_7, sec-C_4H_9, tert-C_4H_9, with $Fe_3(CO)_{12}$ at the first step yield compound $Fe_3(CO)_9(SR)(H)$ which then reacts with the thiol affording compound III. A long heating of tert-C_4H_9SH with $Fe_3(CO)_{12}$ produces the mixture of products: [tert-$C_4H_9SFe(CO)_3]_2$, (tert-$C_4H_9S)_2$, $Fe_3(CO)_9$; (tert-$C_4H_9)_2(S)Fe_4(CO)_{12}$ and $Fe_3(CO)_9S_2$ [19—20].

In these classes of compounds the carbonyl groups substitution reactions have been most investigated. Depending on the ligand and experimental conditions one may substitute one, two or three carbonyls in compounds I and II. The ligands employed were tertiary phosphines, arsines and stibines [21], pyridine, acetonitrile, α,α'-dipyridyl and *o*-phenanthroline [22]. Symmetric and asymmetric derivatives of the respective phosphines, arsines and stibines have been prepared for $[RSFe(CO)_3]_2$ [21,23—26]. The only example of diene (dicyclo-(2,2,1)-heptadiene-2) introduction into bis(methylthioirontricarbonyl) has been described in [17].

Results and discussion

We found that elementary sulfur reacts with iron carbonyls in benzene solution for 1—2 h at 80°C yielding FeS as the main product and negligible amounts of the sulfur-containing cluster complexes I and II in the ratio as 1 : 3 (2—5%).

$$S_8 + Fe_x(CO)_y \rightarrow S_2Fe_2(CO)_6 + S_2Fe_3(CO)_9 + FeS + CO \qquad (1)$$

where $x = 1, y = 5; x = 2, y = 9; x = 3, y = 12$.

Under milder conditions (50—60°C, C_6H_6, 6 h, atomic ratio Fe : S = 1 : 1) in the case of $Fe_3(CO)_{12}$ the total yield of compounds I and II attains 50%: The weight ratio of I : II is 1 : 2 for $Fe_2(CO)_9$ and 1 : 1 for $Fe_3(CO)_{12}$ [27].

Passing H_2S through the solution of $Fe_3(CO)_{12}$ in benzene at 50—55°C gives compound I as the primary product [28]:

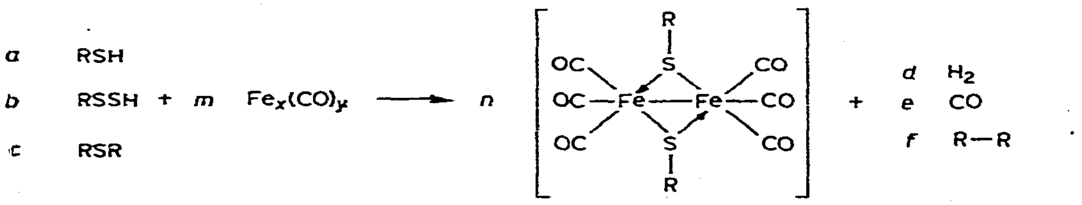
$$H_2S + Fe_3(CO)_{12} \rightarrow S_2Fe_2(CO)_6 \qquad (2)$$

The generated I then reacts with the $Fe_3(CO)_{12}$ present in the solution affording II:

$$S_2Fe_2(CO)_6 + Fe_3(CO)_{12} \rightarrow S_2Fe_3(CO)_9 \qquad (3)$$

The weight ratio of I : II was 2 : 1. Under these conditions compound I does not react with H_2S and does not convert into II in the absence of $Fe_3(CO)_{12}$. The formation of II from I is obviously common to all iron carbonyl derivatives with sulfuric compounds.

The present work is concerned with the relative reactivities of both iron carbonyls and sulfur-containing compounds, since the information in the literature gives no distinct answer to this problem.



(4)

TABLE 1

THE STOICHIOMETRIC COEFFICIENTS OF Eq. (4)

	$x = 1, y = 5, a = 2, b = 1, c = 2$			$x = 2, y = 9, a = 2, b = 1, c = 2$			$x = 3, y = 12, a = 6, b = 3, c = 6$		
m	2	2	2	1	1	1	1	2	2
n	1	1	1	1	1	1	1	3	3
d	1	—	—	1	—	—	3	—	—
e	4	4	4	3	3	3	6	6	6
f	—	—	1	—	—	1	—	—	3

All reactions were carried out with stoichiometric quantities of the starting substances in the thiophene-free benzene solution at 80°C under nitrogen atmosphere. Here and further the reaction course was controlled by means of thin-layer chromatography on plates with fixed silicagel layer.

No quantitative analysis of CO and H_2 was performed: in all cases the presence of CO was detected qualitatively. The respective hydrocarbons generated in reactions with sulfides were identified by gass chromatography.

The molar ratio of reagents, reaction time and yields of the respective compounds (III) per the initial organosulfur compound are listed in Table 2.

Besides the products shown in the general scheme the reaction of thiols with $Fe(CO)_5$ also gives some quantity of the respective disulfide generated via an oxidative coupling of thiols under the action of $Fe(CO)_5$. When $Fe_3(CO)_{12}$ was used the reaction mixture always contained in negligible amount of $Fe(CO)_5$. Its formation was probably due to an interaction of $Fe(CO)_4^*$ particle with the active carbon monoxide produced. Special experiments showed that under such conditions the generated $[RSFe(CO)_3]_2$ does not change.

It is seen from Table 2 that $Fe_3(CO)_{12}$ is most active while $Fe(CO)_5$ is least active.

$$Fe(CO)_5 < Fe_2(CO)_9 < Fe_3(CO)_{12}$$

The reactivity increase in this series is in good agreement with an assumption that activity of iron carbonyls depends on the rate of formation of amount of the coordinatively unsaturated intermediate compound $Fe(CO)_4^*$ [29,30].

TABLE 2

REACTION OF ORGANOSULFUR COMPOUNDS WITH IRON CARBONYLS, FORMATION OF $[RSFe(CO)_3]_2$

Organosulfur compound	$Fe(CO)_5$			$Fe_2(CO)_9$			$Fe_3(CO)_{12}$		
	Reagent ratio	Time (h)	Yield of III (%)	Reagent ratio	Time (h)	Yield of III (%)	Reagent ratio	Time (h)	Yield of III (%)
RSH[a]	1 : 1	22	59—61	2 : 1	11	90—93	3 : 1	1	92—9
RSSR[b]	1 : 2	34	54—59	1 : 1	19	65—67	1.5 : 1	5	72—7
RSR[c]	1 : 1	36	23—25	2 : 1	24	50—54	3 : 1	18	60—6

[a] R = ethyl, n-butyl, n-hexyl, n-octyl, n-dodecyl, phenyl, benzyl. [b] R = n-butyl, n-amyl, n-hexyl, n-dodecyl.
[c] R = methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-dodecyl, cyclopentyl, phenyl.

Since the yields of $[RSFe(CO)_3]_2$ compounds are not affected essentially by the hydrocarbon radical in the organosulfur compounds investigated, their relative reactivities were studied for the mixture of hexanethiol, dihexyldisulfide, and dihexylsulfide. For this purpose we used the method of concurrent reactions [31]: simultaneous interaction of thiol, disulfide and sulfide with $Fe_3(CO)_{12}$ in quantities insufficient for their complete conversion.

$$\begin{array}{llll} 6\ RSH & & & 3\ H_2 \\ 3\ RSSR & + 2\ Fe_3(CO)_{12} \rightarrow & 3[RSFe(CO)_3]_2 + & 6\ CO \\ 6\ RSR & & & 3\ R\text{-}R \end{array} \qquad (5)$$

Concentrations of the organosulfur compounds in the starting mixture and after certain time periods in the reaction mixture were determined by the GLC method. The chromatograms were qualitatively decoded using the internal standard (n-octane) method [32]. The plot of concentration of the organosulfur compounds versus reaction time enables us to determine the relative reactivities of the organosulfur compounds with $Fe_3(CO)_{12}$ computed for $\tau = 60$ min in the following relative units (Fig. 1).

$$\begin{array}{ccccc} RSR & < & RSSR & < & RSH \\ 1 & & 9 & & 13 \end{array}$$

Thus the data listed in Table 1 are in good agreement with the results on relative reactivities of the organosulfur compounds determined by the method of concurrent reactions.

At present it seems not possible to provide an unequivocal explanation for the relative reactivities of organosulfur compounds in reactions with iron carbonyls owing mainly to two reasons. Firstly the site of ligand attack at the metal or at the CO group is not clear although data are available that confirm the possibility of both mechanisms [33]. Secondly it is not definite which step is decisive in generating the bridge-like sulfidosubstituted complexes, namely complex formation of carbonyl dissociation.

Many binuclear carbonyl complexes are known in which an alkylthio group is combined with two metal atoms. Probably the formation of binuclear thioalkylcarbonyl complexes proceeds via the step of intermediate monomeric compounds in which a free electron pair at the sulfur atom possesses sufficient donor

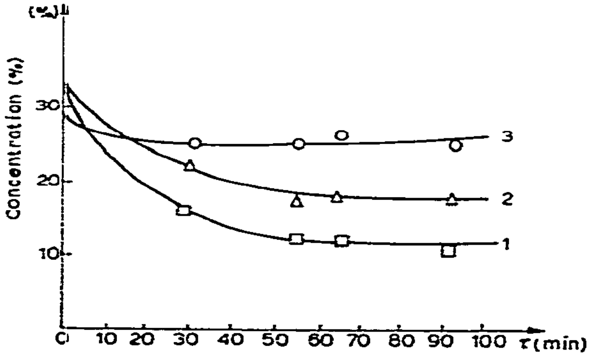


Fig. 1. Concentration of organosulfur compounds versus reaction time. 1, hexanethiol; 2, dihexyldisulfide; 3, dihexylsulfide.

property to replace the CO from another monomeric molecule and produce the dimer [34]. When the donor ability of sulfur reduces upon introduction of the strong electron attractive groups one may isolate and specify the mononuclear complexes [35,36].

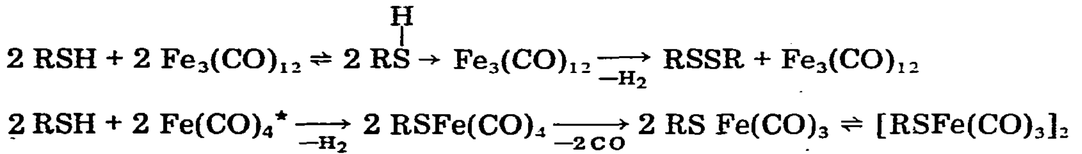
Heiter [37] assumes that the different behaviour of the mono- and binuclear metal carbonyls towards disulfides may be due to a relatively easy ligand cleavage and the carbonyl ligand substitution. In reactions of binuclear carbonyls both steps occur under the same conditions and are usually not separated while in the mononuclear carbonyls there first occurs the carbonyl groups substitution and then under more drastic conditions a combined ligand cleaves. At least partially this difference could be a result of relative ease of the disulfide reduction to the respective sulfidic anionic ligands at an electron-rich metal—metal bond always present in the binuclear metal carbonyls. The mononuclear carbonyls and their intermediate complexes do not have readily available electrons and probably under these conditions after the ligand addition the temperature is allowed to increase up to the point where a homolitic cleavage of joined ligand takes place.

We found that the stoichiometric amounts of alkanethiol and $Fe_3(CO)_{12}$ at room temperature in n-heptane solution (for n-octanethiol) afford the following products: bis(n-octylthioirontricarbonyl), 70%; dioctyldisulfide, 30%; and 30% of unreacted $Fe_3(CO)_{12}$. In this case not even traces of $Fe(CO)_5$ were observed in the reaction mixture.

$$6\ RSH + 2\ Fe_3(CO)_{12} \rightarrow 3[RSFe(CO)_3]_2 + 6\ CO + 3\ H_2 + (RSSR + Fe_3(CO)_{12}) \qquad (6)$$

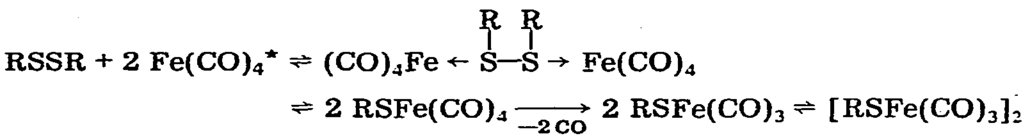
Thus 70% of octanethiol converts into bis(octylthioirontricarbonyl) and 30% of the thiol yields the respective disulfide under the action of the unreacted $Fe_3(CO)_{12}$. Hence under these conditions $Fe_3(CO)_{12}$ is an effective catalyst of thiol oxidation to disulfide. The results obtained manifest that in this case two parallel reaction proceed: the thiol coordination with $Fe_3(CO)_{12}$ and further recombination of thiol fragments into the disulfide as well as thiol coordination with $Fe_3(CO)_{12}$ giving $[RSFe(CO)_3]_2$.

From the data available the following scheme could be proposed for reactions of sulfuric compounds with iron carbonyls:



$$2\ RSH + 2\ Fe_3(CO)_{12} \rightleftharpoons 2\ R\overset{H}{\overset{|}{S}} \rightarrow Fe_3(CO)_{12} \xrightarrow[-H_2]{} RSSR + Fe_3(CO)_{12}$$

$$2\ RSH + 2\ Fe(CO)_4^* \xrightarrow[-H_2]{} 2\ RSFe(CO)_4 \xrightarrow[-2\,CO]{} 2\ RS\ Fe(CO)_3 \rightleftharpoons [RSFe(CO)_3]_2 \qquad (7)$$



$$RSSR + 2\ Fe(CO)_4^* \rightleftharpoons (CO)_4Fe \leftarrow \overset{R}{\overset{|}{S}}-\overset{R}{\overset{|}{S}} \rightarrow Fe(CO)_4$$

$$\rightleftharpoons 2\ RSFe(CO)_4 \xrightarrow[-2\,CO]{} 2\ RSFe(CO)_3 \rightleftharpoons [RSFe(CO)_3]_2 \qquad (8)$$

$$2\ R_2S + 2\ Fe(CO)_4^* \rightleftharpoons 2\ R_2S \rightarrow Fe(CO)_4 \xrightarrow[-(R-R)]{} 2\ RSFe(CO)_4 \xrightarrow[-2\,CO]{} 2\ RSFe(CO)_3$$

$$\rightleftharpoons [RSFe(CO)_3]_2 \qquad (9)$$

It is known that one of the best methods of the synthesis of $Fe_3(CO)_{12}$ is the treatment of $Fe(CO)_5$ with aqueous triethylamine followed by acidification with HCl [38] or H_2SO_4 [39]. Thus it was interesting to react the organosulfur compounds with triethylammonium salt of the trinuclear iron hydridocarbonyl. For alkanethiols no formation of $Fe(CO)_5$ was observed and the respective $[RSFe(CO)_3]_2$ was obtained quantitatively although the reaction time increased from 1 to 3.5 h with respect to $Fe_3(CO)_{12}$.

$$6\,RSH + 2(C_2H_5)_3N \cdot H_2Fe_3(CO)_{11} \rightarrow 3[RSFe(CO)_3]_2 + 2\,(C_2H_5)_3N + 4\,CO + 5\,H_2 \qquad (10)$$

This convenient method may find preparative application owing to the relatively available $Fe(CO)_5$ and almost quantitative regeneration of triethylamine as well as due to the relatively low activity of the latter in the CO substitution in most ironcarbonyl complexes. In our opinion this salt may be used for preparation of various lower valent iron complexes.

The behaviour of $[RSFe(CO)_3]_2$ depending on the temperature is an important characteristic of such compounds. We performed thermal transformation of $[RSFe(CO)_3]_2$ under different conditions: in solution in the presence of both atms

atmospheric oxygen and inert atmosphere; we also determined their thermal stability by the thermogravimetric method.

$[RSFe(CO)_3]_2$ decomposition was carried out in n-dodecane solution at 160—180°C for 2 h by passing pure nitrogen or dry air through the solution. In both cases intensive CO evolution was observed. In the inert atmosphere the reactions yield metallic iron, iron sulfide and almost quantitatively the respective dialkylsulfide:

$$[RSFe(CO)_3]_2 \xrightarrow[\Delta]{N_2} RSR + FeS + Fe + 6\,CO \qquad (11)$$

In the presence of atmospheric oxygen decomposition of these compounds gives the respective dialkyldisulfidies and ferric oxide in quantitative yield. GLC analysis showed not even traces of the sulfide:

$$[RSFe(CO)_3]_2 \xrightarrow[\Delta]{1.5\,O_2} RSSR + Fe_2O_3 + 6\,CO \qquad (12)$$

Thus the behaviour of $[RSFe(CO)_3]_2$ solutions upon decomposition in inert atmosphere and in atmospheric oxygen is essentially different.

Thermal decomposition of the mixture of two different compounds $[RSFe(CO)_3]_2$ and $[R'SFe(CO)_3]_2$ under similar conditions gives asymmetric disulfide along with the respective symmetric disulfides:

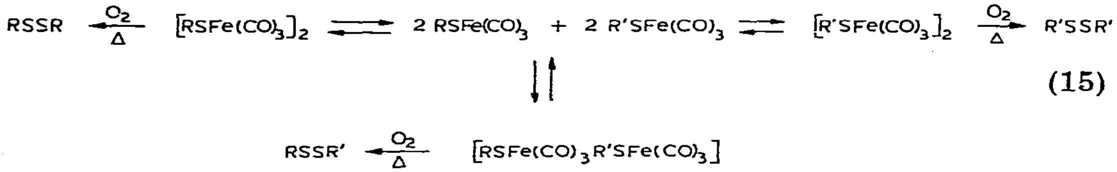
$$2([RSFe(CO)_3]_2 + [R'SFe(CO)_3]_2) \xrightarrow[\Delta]{6\,O_2} RSSR + R'SSR' + RSSR' + 4\,Fe_2O_3 + 24\,CO \qquad (13)$$

An alternative pattern is observed in the reaction of $Fe_3(CO)_{12}$ with mixtures of thiols, disulfides or sulfides, e.g.

$$3(RSH + R'SH) + 2\ Fe_3(CO)_{12} \rightarrow [RSFe(CO)_3R'SFe(CO)_3] + [RSFe(CO)_3]_2 + [R'SFe(CO)_3]_2 + 6\ CO + 3\ H_2. \quad (14)$$

On the basis of the results available the following schemes could be proposed for these reactions.

Decomposition of the mixture $[RSFe(CO)_3]_2$ and $[R'SFe(CO)_3]_2$:



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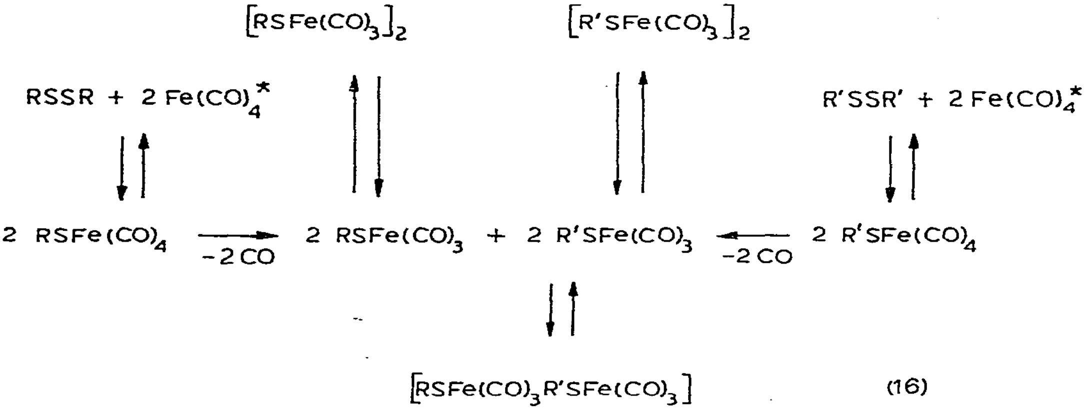
Reaction of mixture of RSSR and R'SSR' with $Fe_3(CO)_{12}$:



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For bis(alkyl-, arylthioirontricarbonyls) thermal stability was investigated by the method of thermogravimetric analysis.

The thermograms of $[RSFe(CO)_3]_2$ have a common pattern. However the DTA of crystalline compounds first display the endothermal effect corresponding to fusion of the compound while oily compounds exhibit no such effect.

As an example let us consider the thermogram of bis(amylthioirontricarbonyl) at 25—300°C (Fig. 2). The decomposition proceeds endothermally with heat absorption at 110—200°C and shows two steps in decomposition rate. From the weight change detected, 4 CO groups eliminate up to 180°C, then two CO groups and the respective disulfide cleave to 210°C. The first step of CO elimination involved heat absorption with a maximum at 120°C; the second step was also endothermal with a maximum at 195°C. At 210°C the decarbonylation is complete which corresponds to a 36% weight change (computed change is 34.6%) and the final product is Fe_2O_3 at the thermogravimetric analysis in atmospheric oxygen. To compare thermal stabilities of $[RSFe(CO)_3]_2$ the temperature of the starting decomposition, formation of volatile products (the so-called TTN temperature) was calculated from thermograms. This value was proposed by Reich and Levi [40] as a criterion of thermal stability of organic compounds. Thermal stabilities of investigated compounds $[RSFe(CO)_3]_2$: R = methyl, 73°; benzyl, 82°; cyclopentyl, 85°; ethyl, 98°; n-propyl, 105°;

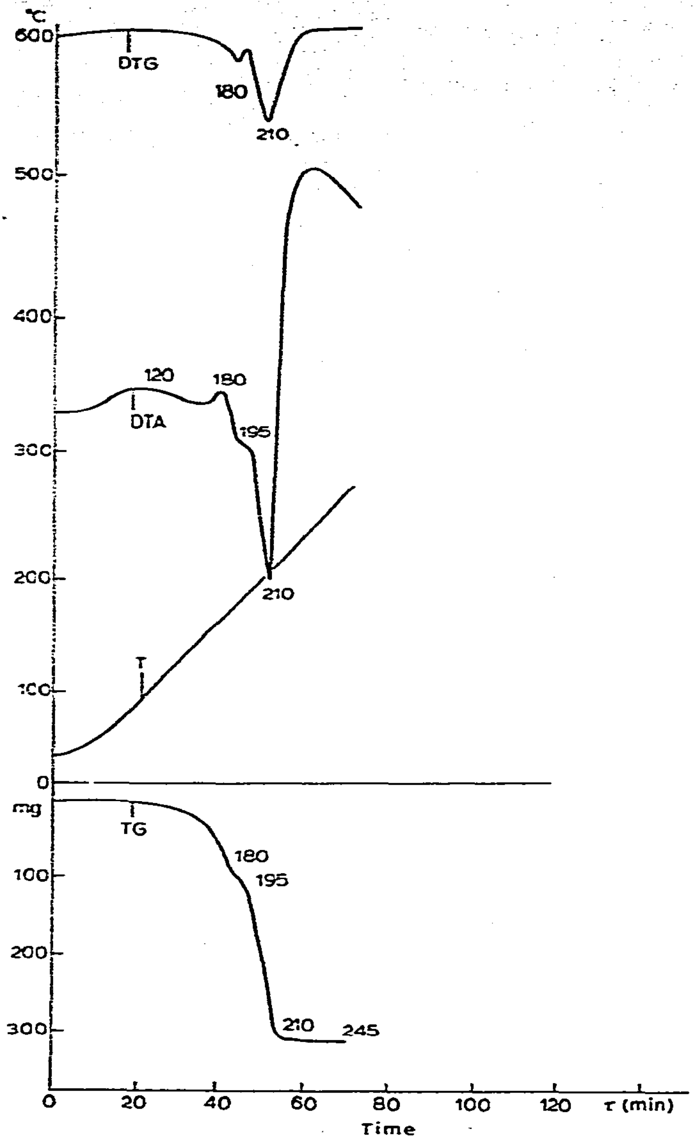


Fig. 2. Thermogram of $[C_5H_{11}SFe(CO)_3]_2$.

n-butyl, 112°; n-amyl, 113°; n-hexyl, 117°; n-dodecyl, 125°; phenyl, 129°C.

The data of mass-spectrometric study by the authors [41] for $[RSFe(CO)_3]_2$ are identical and manifest an ease of loss of six CO groups under electron impact. These results as well as the thermogravimetric measurements serve as evidence that the C—O bond is more stable than the Fe—C in $[RSFe(CO)_3]_2$.

Thermal action for elimination of the irontricarbonyl group is not the only example. To date an oxidative decomposition of a great number of dieneirontricarbonyl complexes under action of different agents has been studied in great detail, e.g. [42,43].

We found that $FeCl_3$ unlike $CuCl_2$ does not decompose $[RSFe(CO)_3]_2$. Treatment of RSFe(CO)$_3{}_2$ with cupric chloride under mild conditions affords the respective dialkyldisulfide in quantitative yield:

$$[RSFe(CO)_3]_2 + 4\ CuCl_2 \xrightarrow[C_6H_6]{80°C} RSSR + 2\ Cu_2Cl_2 + 2\ FeCl_2 + 6\ CO \qquad (17)$$

A concentrated solution of H_2O_2 partially decomposes $[RSFe(CO)_3]_2$ to the respective disulfides. Action of concentrated HNO_3 on $[C_4H_9SFe(CO)_3]_2$ at room temperature gave dibutyldisulfide quantitatively. Analysis of the reaction mixture showed that anti-isomer is most stable from two bis(butylthioisotricarbonyl) isomers. Concentrated HNO_3 in excess gives alkylsulfoacid quantitatively, this being identified in the form of its sodium salt. As one would have expected in this case the reaction occurs via the step of dialkyldisulfide formation:

$$[RSFe(CO)_3]_2 + 12\ HNO_3 \rightarrow 2\ RSO_3H + 2\ Fe(NO_3)_3 + 6\ CO + 6\ NO + 6\ H_2O \qquad (18)$$

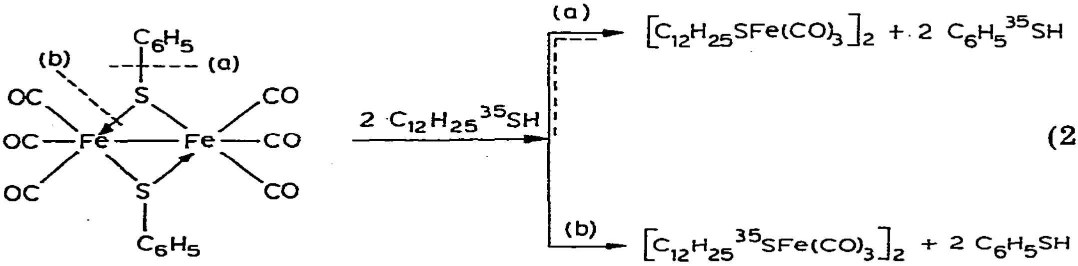
Decomposition of $[RSFe(CO)_3]_2$ to thiols in the presence of HCl was first described in [14]. The reduction of substituted bis(alkylthioiron tricarbonyls) of the type $[RSFe(CO)_2PPh_3]_2$ with sodium amalgam or $NaBH_4$ leads to the salts of polynuclear carbonylferrates and sodium mercaptides [21]. We found that the action of $LiAlH_4$ ethereal solution in excess converted $[RSFe(CO)_3]_2$ quantitatively into the respective thiols avoiding the formation of polynuclear ironcarbonyl salts:

$$[RSFe(CO)_3]_2 \xrightarrow{LiAlH_4} 2\ RSH + 2\ Fe + 6\ CO \qquad (19)$$

No data are known in the literature on the substitution of heteroligand in such complexes. We showed that $[RSFe(CO)_3]_2$ undergo exchange with various thiols [44]. Independently of the hydrocarbon radical structure both in the starting bis(alkylthioirontricarbonyl) and in the thiol molecule an exchange reaction occurs:

$$\underset{syn,\ anti}{[RSFe(CO)_3]_2} + 2\ R'SH \rightleftharpoons \underset{syn,\ anti}{[RS'Fe(CO)_3]_2} + 2\ RSH \qquad (20)$$

Since it is difficult to separate *syn* and *anti* isomers of the starting and generated bis(alkylthioirontricarbonyls) the exchange was studied in more detail for bis(phenylthioirontricarbonyl), which is a single isomer and its R_f is essentially different from the *syn* and *anti* isomers of $[H\text{-}C_{12}H_{25}SFe(CO)_3]_2$. Use of dode-



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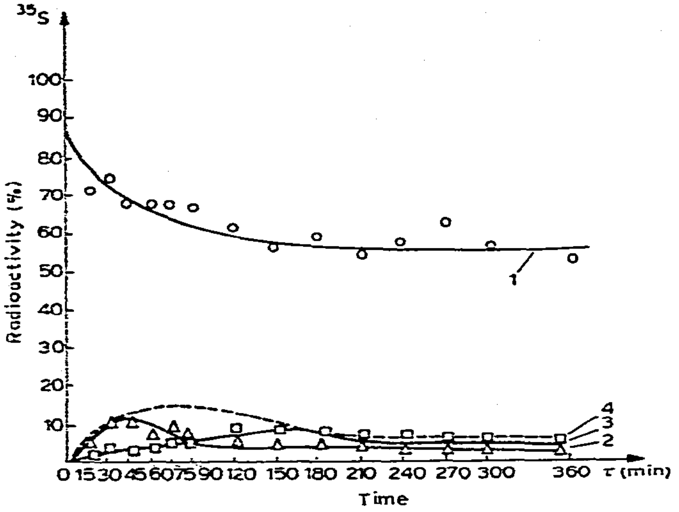


Fig. 3. Radioactivity of organosulfur compounds versus reaction time. 1, $C_{12}H_{25}{}^{35}SH$; 2, *syn*-$[C_{12}H_{25}{}^{35}SFe(CO)_3]_2$; 3, *anti*-$[C_{12}H_{25}{}^{35}SFe(CO)_3]_2$; 4, *syn*- + *anti*-$[C_{12}H_{25}{}^{35}SFe(CO)_3]_2$.

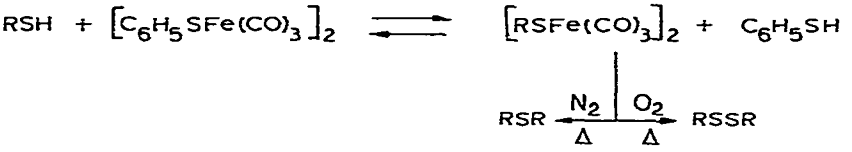
canethiol labeled with radioactive sulfur-35 was helpful in solving this problem of elucidating the bond cleavage. The reaction was carried out in absolute methanol at 65°C in an inert atmosphere for 6 h. The reaction course was controlled by TLC.

If the cleavage occurs at the C—S (a) bond then in the reaction with dodecanethiol riched with ^{35}S one should observe the formation of $C_6H_5{}^{35}SH$ and $[C_{12}H_{25}SFe(CO)_3]_2$ while the cleavage at the Fe—S (b) bond should result in the formation of $[C_{12}H_{25}{}^{35}SFe(CO)_3]_2$ and C_6H_5SH.

It was shown that the exchange involves the cleavage of the Fe—S bond. Analysis of the exchange reaction mixture components reveals that at first the $C_{12}H_{25}{}^{35}SH$ concentration decreases while that of $[C_{12}H_{25}{}^{35}SFe(CO)_3]_2$ gradually increases. The formation of the *syn* isomer is faster than that of the *anti* species.

It is seen from Fig. 3 that an equilibrium is reached in 3.5 h.

The results of this exchange reaction with an account of the thermal stability of the respective bis(alkylthioirontricarbonyls) could be employed for the transformation of the low molecular weight thiols into disulfides or sulfides.



$$RSH + [C_6H_5SFe(CO)_3]_2 \rightleftharpoons [RSFe(CO)_3]_2 + C_6H_5SH \qquad (22)$$

$$RSR \xleftarrow[\Delta]{N_2} [RSFe(CO)_3]_2 \xrightarrow[\Delta]{O_2} RSSR$$

$R = CH_3, C_2H_5; C_3H_7$

Thus by investigating the properties of bis(alkyl-, arylthioirontricarbonyls) new methods of organosulfur compound preparation were established. Depending on the reaction conditions one may obtain the respective thiols, disulfides and sulfides quantitatively in the pure form.

Experimental

Adsorption and gas liquid chromatography were used for analysis of the reaction mixtures and compound identification. Adsorbents for the thin layer chromatography (TLC) were Woelm silicagel and Kavalier Silufol plates. The eluents were n-hexane or petroleum ether (b.p. 40—70°C).

The gas-liquid chromatographic (GLC) analysis of the thermal transformations of bis(alkyl-, arylthioiron tricarbonyls) was performed on a LKhm-8MD chromatograph with catarometer as heat conductivity detector, column length 3 m, diameter 3 mm. Polyethyleneglycol PEG 15000 was used as stationary phase as it is most selective for sulfides, disulfides and thiols among the stationary phases of different polarities [45] on chromosorb W, and nitrogen at a rate of 20 ml/min was used as gas carrier.

In the study of relative reactivities of the organosulfur compounds the GLC analysis was performed on a Tsvet-101 chromatograph with a flame-ionization detector under temperature linear programming at 120—230°C at a rate of 20 deg./min. The high programming rate was governed by the broad b.p. range of the reaction components. 10% apieson L on chromosorb W was used as the stationary phase. The glass column length was 2 m, diameter 3 mm. Helium was used as gas carrier at a rate of 40 ml/min.

Thermal stability was studied by the thermogravimetric method under air on F. Paulik, I. Paulik and L. Erday's derivatigraph. 600 mg samples were used at a heating rate of 3 degr./min. Alumina was used as standard.

The IR spectra were recorded on a UR-20 spectrophotometer in KBr pellets or liquid films.

The mass spectra were recorded on LKB-2091 gas-chromato-mass-spectrometer with direct input into ion source at evaporation temperature 70°C and 70 eV ionization energy.

Preliminary purified commercial products (liquids were distilled, solids crystallized) manufactured at KhRK plant or those prepared by known procedures were employed and their constants are in agreement with the literature data [46]. GLC analysis detected 96—99% purity of the initial sulfuric compounds.

All reactions were carried out under dry and pure nitrogen. Iron pentacarbonyl was used in the form of the commercial product, diiron nonacarbonyl obtained by the literature method [47], triethylammonium salt of triironundecacarbonyl hydride prepared as in [48], and triirondodecacarbonyl synthesized according to [39].

Reaction of elementary sulfur with ironcarbonyls

A mixture of 0.02 mol of amorphous elementary sulfur (m.p. 120°C) and 0.02 mol of the respective ironcarbonyl was stirred in 100 ml of absolute benzene at 80°C for 2 h (for $Fe(CO)_5$), 1.5 h (for $Fe_2(CO)_9$) and 1 h (for $Fe_3(CO)_{12}$). Iron sulfide was filtered off (90—95% per S_8). After benzene removal a mixture of $S_2Fe_2(CO)_6$ (I) and $S_2Fe_3(CO)_9$ (II) (2—5% per S_8) (1 : 3) was obtained. 0.4 g of clusters (I) and (II) chromatographed on silicagel (hexane eluent) gave 0.1 g of I, m.p. 45—46°C. IR spectrum (ν(CO), cm^{-1}): 2081, 2042, 2005. Found: C, 20.76; Fe, 32.24; S, 18.52. $C_6Fe_2S_2O_6$ calc.: C, 20.93; Fe, 32.48; S, 18.65%,

TABLE 3

[RSFe(CO)$_3$]$_2$ ELEMENTAL ANALYSIS AND IR SPECTRAL DATA

Nos.	R	Colour	M.p. (°C)	Found (calcd.) (%)				Gross formula	IR spectrum, ν(CO) (cm^{-1})
				C	H	S	Fe		
1	CH_3 (*syn*) (*anti*)	orange red	102–103 [a] 65–66	25.56 (25.70)	1.60 (1.62)	16.96 (17.17)	29.96 (29.84)	$C_8H_6S_2Fe_2O_6$	2080, 2042, 2000, 1996
2	C_2H_5	deep red	75–76 [b]	29.65 (29.87)	2.52 (2.50)	15.82 (15.95)	27.65 (27.83)	$C_{10}H_{10}S_2Fe_2O_6$	2075, 2035, 2002, 1990
3	n-C_3H_7	red	oil	33.65 (33.55)	3.22 (3.28)	14.66 (14.90)	25.85 (25.97)	$C_{12}H_{44}S_2Fe_2O_6$	2070, 2033, 2000, 1985
4	n-C_4H_9	orange-red	oil	36.90 (36.72)	3.94 (3.96)	14.07 (13.99)	24.20 (24.39)	$C_{14}H_{18}S_2Fe_2O_6$	2080, 2035, 1999, 1986
5	n-C_5H_{11}	"	oil	39.61 (39.53)	4.52 (4.56)	13.18 (13.19)	23.02 (22.97)	$C_{15}H_{22}S_2Fe_2O_6$	2075, 2036, 2000, 1987
6	n-C_6H_{13}	"	oil	42.30 (42.05)	5.06 (5.08)	12.70 (12.47)	21.94 (21.72)	$C_{18}H_{26}S_2Fe_2O_6$	2072, 2038, 2001, 1988
7	n-$C_{12}H_{25}$	carmine-red	oil	52.87 (52.70)	7.32 (7.38)	9.27 (9.40)	15.80 (16.37)	$C_{30}H_{50}S_2Fe_2O_6$	2066, 2035, 1998, 1985
8	C_5H_9	red-orange	oil	40.32 (40.00)	3.62 (3.68)	13.32 (13.29)	23.35 (23.18)	$C_{16}H_{18}S_2Fe_2O_6$	2071, 2032, 2000, 1982
9	C_6H_5	brick red	140–141 [c]	43.55 (43.41)	2.01 (2.02)	12.74 (12.88)	22.62 (21.42)	$C_{18}H_{10}S_2Fe_2O_6$	2074, 2036, 2003, 1986
10	$C_6H_5CH_2$	dark red	91–92	45.20 (45.66)	2.55 (2.68)	(12.36 (12.19)	21.36 (21.23)	$C_2H_{14}S_2Fe_2O_6$	2074, 2034, 2001, 1984

[a] m.p. 65–67.5° [16], [b] m.p. 75.5° [13], [c] m.p. 140°C [15].

m/e 344. The data of [3]: m.p. 46.5°C. 0.28 g of II, m.p. 114°C was also isolated. IR spectrum (ν(CO), cm^{-1}): 20.62, 2045, 2024, 1985. Found: C, 22.24; Fe, 34.40; S, 13.20. $C_9Fe_3S_2O_9$ calc.: C, 22.32; Fe, 34.69; S, 13.21%, *m/e* 484. The data of [3]: m.p. 114°C.

Reaction at 50—60°C for 6 h gave (atomic ratio of Fe : S = 1 : 1) 50% of I and II for $Fe_3(CO)_{12}$. Weight ratio of I : II is 1 : 2 for $Fe_2(CO)_9$ and 1 : 1 for $Fe_3(CO)_{12}$.

Reaction of H_2S with $Fe_3(CO)_{12}$

885 ml (1.36 g, 0.04 mol) of H_2S prepared by the nonacidic method [49] was passed through a solution of 10.08 g (0.02 mol) of $Fe_3(CO)_2$ in 100 ml of C_6H_6 at 80°C for 30—40 min. The mixture was cooled, filtrated from FeS and the solvent removed. 0.7 g (11% per H_2S) of $S_2Fe_2(CO)_6$ and obtained. At 50—55°C the primary product is $S_2Fe_2(CO)_6$. The weight ratio of I : II is 2 : 1. Mixed samples of the products prepared by reactions of iron carbonyls with S and H_2S give no depression of m.p. with authentic samples obtained by the procedures of [3].

Synthesis of bis(alkyl-, arylthioiron tricarbonyls) (general method)

All reactions were carried out with stoichiometric amounts of the initial compounds in absolute benzene at its b.p. The reaction course was controlled by means of TLC on silicagel. The reaction mixture was filtrated, the solvent evaporated, and teh residue chromatographed on silicagel column (n-hexane eluent).

In some cases the unreacted organosulfur compounds were separated from $[RSFe(CO)_3]_2$ by steam distillation, since starting with R = C_4 and higher, bis(alkylthioirontricarbonyls) practically could not be distilled.

Reaction time, yield of $[RSFe(CO)_3]_2$ per initial organosulfur compound and the molar ratios of reagents are listed in Table 2.

The constants, data of elemental analysis and IR spectra for $[RSFe(CO)_3]_2$ obtained are shown in Table 3.

Reaction of the mixture of $C_6H_{13}SH$, $(C_6H_{13}S)_2$ and $(C_6H_{13})_2S$ with $Fe_3(CO)_{12}$

A mixture of 7.08 g (0.06 mol) of $C_6H_{13}SH$, 7.02 g (0.03 mol) of $(C_6H_{13}S_2)$, 12.12 g (0.06 mol) of $(C_6H_{13})_2S$, 1.14 g (0.01 mol) of n-octane and 10.08 g (0.02 mol) of $Fe_3(CO)_{12}$ in 100 ml of n-decane was stirred at 80°C for 2 h. Concentrations of sulfuric compounds in the mixture of the initial moment and after 15, 30, 55, 65, 90 and 120 min were determined by GLC. Concentrations of the organosulfur compounds in the starting mixture are: for $C_6H_{13}SH$, 32.25%; for $(C_6H_{13}S)_2$, 32.16%; for $(C_6H_{13})_2S$, 27.77%. For $\tau = 60$ min the concentrations of the organosulfur compounds remaining in the mixture were computed: for $C_6H_{13}SH$, 11.01%; for $(C_6H_{13}S)_2$, 17.52%; for $(C_6H_{12})_2S$, 26.17%. Thus in 60 min the reacted quantities are 1.60% of $(C_6H_{13})_2S$, 14.25% of $(C_6H_{13}S)_2$ and 21.24% of $C_6H_{13}SH$. If the reacted quantity of $(C_6H_{13})_2S$ is taken as unity then the amounts of reacted $(C_6H_{13}S)_2$ and $C_6H_{13}SH$ are 9 and 13 relative units respectively.

Reaction of $C_8H_{17}SH$ with $Fe_3(CO)_{12}$ at room temperature

A mixture of 0.1 ml (0.0876 g, 0.6 mmol) of $C_8H_{17}SH$, 0.1 g (0.2 mmol) of $Fe_3(CO)_{12}$ and 60 ml of n-heptane was stirred at room temperature for 24 h. Then 0.03 g of unreacted $Fe_3(CO)_{12}$ was separated by freezing (—78°C). After evaporation of the solvent at low pressure 0.15 g of the mixture containing 0.132 g (69.5% per initial thiol) of $[C_8H_{17}SFe(CO)_3]_2$ and 0.018 g (100% per remaining thiol) of $(C_8H_{17}S)_2$ was obtained.

Reaction of n-$C_{12}H_{25}SH$ with $C_2H_5NH \cdot HFe_3(CO)_{11}$

A mixture of 1.44 ml (1.21 g, 0.006 mol) of dodecanethiol, 1.16 g (0.002 mol), of $C_2H_5NH \cdot HFe_3(CO)_{11}$ and 50 ml of C_6H_6 was stirred at 80°C for 3.5 h. The generated bis(dodecylthioirontricarbonyl) was isolated as described. 1.89 g (92% per $C_{12}H_{25}SH$) of $[C_{12}H_{25}SFe(CO)_3]_2$. Found: C, 52.87; H, 7.32; S, 9.27. $C_{30}H_{50}Fe_2S_2O_6$ calc.: C, 52.79; H, 7.38; S, 9.40%. Analogously the following compounds were obtained: $[RSFe(CO)_3]_2$ where R = ethyl, n-butyl, n-hexyl and phenyl. The constants and yields of the compounds obtained correspond to those prepared from $Fe_3(CO)_{12}$.

Thermal decomposition (general procedure)

Dry and pure nitrogen and air were bubbled through a solution of 0.001—0.002 mol of the respective $[RSFe(CO)_3]_2$ in 50 ml of n-dodecane with slow heating to 160—180°C for 2 h. The end of the reaction was detected by completion of CO evolution. The solid was separated and analyzed after decomposition reactions.

Decomposition under inert atmosphere

0.15 g of the mixture of FeS and Fe and 0.35 g (95%) of $(C_{12}H_{25})_2S$, m.p. 40—41° C, were isolated from 0.68 g (0.001 mol) of $[C_{12}H_{25}SFe(CO)_3]_2$. Found: C, 77.68; H, 13.42; S, 8.56. $C_{24}H_{50}S$ calc.: C, 77.84; H, 13.51; S, 8.65%. The data of [46]: m.p. 40.5—41°C. Analogously the respective sulfides were prepared from $[RSFe(CO)_3]_2$, R = C_4H_9, C_6H_{13}. In all cases not even traces of disulfide was detected in the reaction mixture.

Decomposition in the presence of atmospheric oxygen

0.68 g (0.001 mol of $[C_{12}H_{25}SFe(CO)_3]_2$ gave 0.16 g of Fe_2O_3 and 0.39 g (97%) of $(C_{12}H_{25}S)_2$, m.p. 32—33°C. Found: C, 71.44; H, 12.42; C, 15.86. $C_{24}H_{50}S_2$ calc.: C, 71.57; H, 12.51; S, 15.92%. The data of [46]: m.p. 32°C.

A mixture of 1.0 g (0.002 mol) of $[C_4H_9SFe(CO)_3]_2$ and 1.4 g (0.002 mol) of $[C_{12}H_{25}SFe(CO)_3]_2$ yielded 0.85 g of Fe_2O_3. GLC analysis of the filtrate by "additive" method and TLC analysis by comparison with R_f of authentic samples proved the presence of $(C_4H_9S)_2$, $(C_{12}H_{25}S)_2$ and $C_4H_9SSC_{25}$ in about equivalent quantities. GLC analysis showed in every case the absence of the respective sulfides.

Reaction of mixtures of thiols, disulfides or sulfides with $Fe_3(CO)_{12}$

A mixture of 0.06 mol of C_4H_9SH and 0.06 mol of $C_{12}H_{25}SH$ or 0.03 mol of $(C_4H_9S)_2$ and 0.03 mol of $(C_{12}H_{25}S)_2$ or 0.06 mol of $(C_4H_9)_2S$ and 0.06 mol of $(C_{12}H_{25})_2S$ respectively was stirred in 100 ml of C_6H_6 with 0.02 mol of $Fe_3(CO)_{12}$

at 80°C. Reaction time was 1, 5 and 18 h for thiols, disulfides and sulfides respectively. The reaction mixtures were treated as described above. In all cases the residue was a mixture of *syn* and *anti* isomers of $[C_4H_9SFe(CO)_3]_2$, $[C_{12}H_{25}SFe(CO)_3]_2$ and $(C_4H_9S)(C_{12}H_{25}S)Fe_2(CO)_6$. Repeated chromatography of the reaction mixture on plates with fixed silicagel layer yielded approximately equal quantities of the respective bis(alkylthioirontricarbonyls).

Action of $CuCl_2$

A mixture of 2.29 g (0.005 mol) of $[C_4H_9SFe(CO)_3]_2$ and 2.67 g (0.02 mol) of cupric chloride in 20 ml of absolute benzene was stirred at 80°C for 30 min. The mixture was filtrated, the residue washed with petroleum ether (4 × 5 ml) and 0.88 g of cuprous chloride was obtained. The combined organic solution was washed with water, dried of $MgSO_4$ and after removal of the solvent 0.82 g (92%) of $(C_4H_9S)_2$ was obtained. Analogously this reaction takes place with the following $[RSFe(CO)_3]_2$ compounds: R = C_5H_{11}, C_6H_5, $C_{12}H_{25}$. Constants of the separated dialkyldisulfides corresponded to the literature data [46]. GLC analysis detected the absence of the respective sulfides in the reaction mixtures.

Oxidation with concentrated HNO_3.

3.44 ml (4.72 g, 0.075 mol) of concentrated HNO_3 (d = 1.37 g cm^3) was added dropwise to 3.41 g (0.005 mol) of $[C_{12}H_{25}SFe(CO)_3]_2$ at room temperature. The reaction completion was controlled by disappearance of $[C_{12}H_{25}SFe(CO)_3]_2$ then the mixture was poured into saturated NaCl solution. The solid generated was filtered off, washed with a small quantity of water, and dried in air and under vacuo to constant weight. 2.65 g (98%) of dodecylsulfoacid sodium salt was obtained. Found: C, 51.30; H, 9.36; S, 11.57. $C_{12}H_{26}SO_3$ calc.: C, 51.91; H, 9.25; S, 11.82. IR spectrum (cm^{-1}): $\nu_{as}(SO_2)$, 1260—1150; $\nu_s(SO_2)$, 1070; and ν(S—O) 640.

Analogously this reaction proceeds with $[RSFe(CO)_3]_2$, R = C_4H_9, C_6H_{13}, C_6H_5.

Reduction with $LiAlH_4$

A suspension of 1.9 g (0.05 mol) of $LiAlH_4$ in 20 ml of absolute ether was added with stirring to a solution of 2.29 g (0.005 mol) of $[C_4H_9SFe(CO)_3]_2$ in 10 ml of absolute ether. The reaction was completed upon disappearance of $[C_4H_9SFe(CO)_3]_2$ in TLC, the $LiAlH_4$ excess was decomposed with wet ether and acidified water. The ethereal layer was separated, washed with water and dried over $MgSO_4$. After solvent removal 0.72 g (80%) of C_4H_9SH was obtained, b.p. 98°C, n_D^{20} 1.4424. The data of [46]: b.p. 98.5°C, n_D^{20} 1.4429. Analogously this reaction proceeds with $[RSFe(CO)_3]_2$, R = C_6H_{13}, C_6H_5, $C_{12}H_{25}$, yield 80—90%.

Reaction of $[C_6H_5SFe(CO)_3]_2$ *with* $C_{12}H_{25}{}^{35}SH$

A mixture of 0.249 g (0.5 mmol) of $[C_6H_5SFe(CO)_3]_2$ and 0.24 ml (0.202 g, 1 mmol) of $C_{12}H_{25}{}^{35}SH$ (obtained from radioactive thiourea [50]) in 10 ml of absolute CH_3OH was stirred under argon at 65°C for 6 h. The reaction course was controlled by TLC on plates with fixed silicagel layer (hexane eluent). Radioactivity of some compounds was registered on scintillation counter Mark-2

"Nuclear Chicago" at count efficientcy of 90% ^{35}S. An equilibrium was obtained in 3.5 h. The results obtained on automatic counter after computing the radioactivities of separate compounds (%) are shown in the plot (Fig. 3).

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