SULPHUR-CONTAINING METAL CARBONYLS

VI*. A MIXED COBALT-IRON CARBONYL SULPHIDE

SAMIR A. KHATTAB, LÁSZLÓ MARKÓ, GYÖRGY BOR AND BERNADETTE MARKÓ
Hungarian Oil and Gas Research Institute M.Á.F.K.I., Veszprém (Hungary)

(Received September 24th, 1963)

Recently, it was reported[3] that thiophene does not retard or inhibit the conversion of olefins to aldehydes in oxo-synthesis (hydroformylation). Greenfield and co-workers[4], however, observed that during attempts to hydrogenate the thiophene nucleus to thiolane, in presence of cobalt catalysts, desulphurisation occurred and the catalyst was partly converted to cobalt sulphide and metallic cobalt.

Continuing previous work done in this laboratory[1,2,5], the effect of thiophene on the hydroformylation catalyst $[Co_2(CO)_8]$ was investigated. When thiophene was allowed to react with the synthesis gas mixture (2 CO : 1 H_2) in presence of dicobalt octacarbonyl, under hydroformylation conditions, desulphurisation occurred and the catalyst was partly converted to cobalt sulphide. Working up of the reaction product, proved the partial reduction of thiophene nucleus to thiolane; a result which is in agreement with the findings of Greenfield and co-workers. A poor yield of a mixed cobalt–iron carbonyl derivative (I) was also isolated; this apparently resulted from a reaction between dicobalt octacarbonyl and thiophene on the inner surface of the autoclave under the reaction conditions. This remarkable result caused us to repeat the above reaction, but in presence of a mixture of dicobalt octacarbonyl and iron pentacarbonyl. Desulphurisation of thiophene nucleus again occurred and the two carbonyls were partly converted into cobalt and iron sulphides. Working up of the reaction product, showed a much higher yield of compound (I) than in the first experiment.

Elementary analysis as well as thermal decomposition proved its molecular formula to be $Co_2Fe(CO)_9S$.

Carbonyl compounds containing a metal–metal bond between two different transition metal atoms have only been recently reported[6–10], and as far as we know, dicobalt iron nonacarbonyl sulphide (I) is the first sulphur-containing mixed carbonyl derivative to be reported.

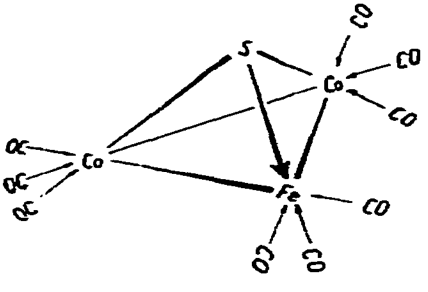
Compound (I) crystallizes in shiny dark violet crystals, which are remarkably air-stable.

Its infrared spectrum (in hexane solution and using a LiF prism) exhibits absorption bands only in the C–O stretching region at 2104.5 (0.8), 2066 (9.0), 2053.5 (10), 2042 (5.5), 2029 (1.8), 2000 (0.2), 1984.5 (2.5) and 1949.5 (0.1) cm^{-1} (accuracy $\pm$ 0.5 cm^{-1}, relative intensities are given in the parentheses), in the metal–carbon stretching and M–C–O bending region at 607, 569, 521, 511, 497 and 444 cm^{-1} (KBr pellet, KBr prism, accuracy $\pm$ 2 cm^{-1}).

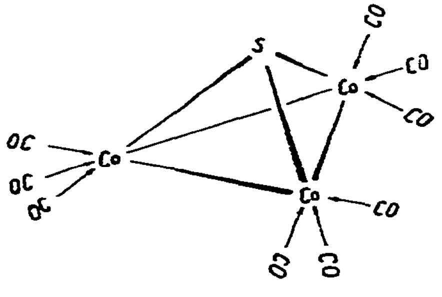
---

[*] For part IV and V see ref. 1 and 2 resp.

A trigonal pyramidal structure is suggested for sulphide (I) which is analogous to that of tricobalt nonacarbonyl sulphide (II) recently prepared in this laboratory[11].



I



II

The suggested structure for sulphide (I) does not involve an unpaired electron on the sulphur atom, a fact which may explain the highly increased stability to oxidation of sulphide (I), compared with that of sulphide (II).

Sulfide (I) was also formed when a mixture of iron and cobalt carbonyls was allowed to react under the same reaction conditions with either elementary sulphur or ethanethiol and synthesis gas. The two carbonyls were again partly converted to cobalt and iron sulphides.

The formation of sulphide (I) under the hydroformylation conditions in presence of cobalt and iron carbonyls always seems to be possible whenever organic sulphur compounds (e.g. ethanethiol and thiophene), which desulphurise under these conditions, are present.

When diiron hexacarbonyl disulphide $[Fe_2(CO)_6S_2]$ (III)[12] was allowed to react with dicobalt octacarbonyl, at room temperature and under atmospheric pressure, cobalt sulphide was deposited and the disulphide (III) was converted into sulphide (I). The infrared spectrum of the reaction product also showed the formation of iron pentacarbonyl, dicobalt pentacarbonyl sulphide $[Co_2(CO)_5S]_n$ (IV)[5], as well as traces of sulphide (II). The following reaction scheme is suggested:

$$Fe_2(CO)_6S_2 + Co_2(CO)_8 \longrightarrow Fe(CO)_5 + Co_2Fe(CO)_9S + [S] .$$

The formation of sulphides (II) and (IV) as well as cobalt sulphide could possibly be explained by the interaction of the hypothetically formed sulphur with dicobalt octacarbonyl[5]. A semi-quantitative determination of the amounts of iron pentacarbonyl and sulphide (I) formed in the reaction, however, showed that the quantity of iron pentacarbonyl is less than expected according to the above mentioned reaction scheme. The stoichiometry of the reaction, therefore, seems to be more complicated.

Triiron nonacarbonyl disulphide $[Fe_3(CO)_9S_2]$ (V)[12] was found to be inert towards dicobalt octacarbonyl under the above mentioned conditions.

The ease of formation of sulphide (I) from disulphide (III) offers a method for the preparation of sulphide (I) under atmospheric pressure.

We would also like to report that a minute amount of another carbonyl derivative (VI) was also formed in the thiophene reaction. The presence of compound (VI) was detected in the infrared spectrum of the last hexane eluates of sulphide (I). Attempts to isolate compound (VI) from sulphide (I) were unsuccessful, because it was being continuously transformed to sulphide (I), even during the recording of the infrared spectrum. Compound (VI) possesses characteristic C–O stretching bands at 2081 (s), 2041 (vvs), 2028 (vs), 2016 (s), 2010 (sh) and 1970 (ms) cm^{-1} (accuracy ± 1 cm^{-1}, in hexane solution). The bands at 2041 and 2028 cm^{-1} were always overlapped by the corresponding bands of sulphide (I).

EXPERIMENTAL

The thiophene used was purified by fractional distillation. The dicobalt octacarbonyl was prepared according to the method previously reported[13]. The experiments with thiophene, elementary sulphur and ethanethiol were conducted in a 500 ml stainless steel, rocking autoclave.

Procedure for thiophene

A mixture of 126.2 g (1.5 mole) thiophene, 12.8 g (0.038 mole) dicobalt octacarbonyl and 7.35 g (0.038 mole) iron pentacarbonyl was placed in the autoclave which was pressurised with synthesis gas (2 CO : 1 H_2) to 185 atm. at room temperature and was then heated to 200° C. After the pressure reached 290 atm., heating was continued for four and half hours. When the reaction period was over, the reaction mixture was allowed to cool and then was filtered from the black deposit (3.4 g; composition: Co, 63.0; Fe, 1.8; S, 30.8%). The filtrate was distilled under vacuum, and the residue after distillation was dissolved in 45 ml of hexane and chromatographed on freshly activated silica gel. The hexane eluates were collected portionwise and infrared spectrum was recorded for each aliquot. The eluates containing pure sulphide (I) were bulked and the solvent was removed by vacuum distillation. The solid residue was crystallised from hexane at —70° to shiny dark violet crystals of sulphide (I); yield, 1.6 g (9.3% based on the cobalt introduced). The last hexane eluates were shown by the infrared spectrum to contain a minute quantity of compound (VI) besides sulphide (I).

Sulphide (I) has no sharp melting point but it undergoes some melting at 107° and begins to decompose at 112° to carbon monoxide, cobalt and iron sulphides. It is remarkably air-stable in its crystalline form, and to a less extent in solutions. It is soluble in common organic solvents to give a reddish brown solution. (Found: Co, 25.8; Fe, 12.3; S, 7.0; C, 23.7; CO, 54.2. $Co_2Fe(CO)_9S$ calcd.: Co, 25.74; Fe, 12.20; S, 7.01; C, 23.53; CO, 55.05%.)

Procedure for elementary sulphur

The reaction was conducted under the same conditions as above using 1.83 g (0.057 mole) elementary sulphur and 126 ml hexane as a solvent. The deposit of cobalt and iron sulphides was filtered off (4.0 g) and the filtrate was worked up as above to yield 0.15 g (0.9% based on the cobalt introduced) of sulphide (I).

Procedure for ethanethiol

The same procedure as in the thiophene experiment was used, but 93.2 g (1.5 mole) of ethanethiol was substituted for the thiophene. The deposit of cobalt and iron sulphides was 3.5 g and the yield of sulphide (I) was 0.475 g (2.8% based on the cobalt introduced).

Reaction of diiron hexacarbonyl disulphide (III) with dicobalt octacarbonyl

199 mg (0.59 mmole) of dicobalt octacarbonyl was added to a solution of 103 mg (0.30 mmole) of disulphide (III) in 25 ml hexane. After being well shaken, the mixture was allowed to stand overnight under nitrogen. A black precipitate (6 mg) was formed and was proved by analysis to be principally cobalt sulphide. The product was filtered under nitrogen and the filtrate was vacuum distilled. The residue was crystallised from hexane at —70° C to yield crystals of sulphide (I) (152 mg, 56%, based on cobalt introduced).

The infrared spectrum of the filtrate before vacuum distillation proved the formation of iron pentacarbonyl (25 mg, 21%, based on iron introduced, as estimated from the spectrum), much smaller amounts of sulphide (IV) and traces of sulphide (II).

Infrared spectra were recorded by a double-beam spectrometer (UR-10 Carl Zeiss, Jena) using the LiF prism.

SUMMARY

Dicobalt iron nonacarbonyl sulphide $Co_2Fe(CO)_9S$ (I) is formed when either thiophene, elementary sulphur or ethanethiol are allowed to react with a mixture of dicobalt octacarbonyl and iron pentacarbonyl under hydroformylation conditions.

This new sulphide (I) was also prepared under atmospheric pressure from diiron hexacarbonyl disulphide and dicobalt octacarbonyl.

REFERENCES

1 L. Markó, G. Bor and E. Klumpp, *Angew. Chem.*, 75 (1963) 248.
2 E. Klumpp, L. Markó and G. Bor, *Chem. Ber.*, under publication.
3 V. Macho, *Chem. Zvesti*, 15 (1961) 181.
4 H. Greenfield, S. Metlin, M. Orchin and I. Wender, *J. Org. Chem.*, 23 (1958) 1054.
5 L. Markó, G. Bor, E. Klumpp, B. Markó and G. Almásy, *Chem. Ber.*, 96 (1963) 955.
6 E. W. Abel, A. Singh and G. Wilkinson, *J. Chem. Soc.*, (1960) 1321.
7 P. Chini, L. Colli and M. Peraldo, *Gazz. Chim. Ital.*, 90 (1960) 1005.
8 J. F. Tilney-Bassett, *Proc. Chem. Soc.*, (1960) 419.
9 R. B. King, P. M. Treichel and F. G. A. Stone, *Chem. Ind. (London)*, (1961) 747.
10 K. K. Joshi and P. L. Pauson, *Z. Naturforsch.*, 17b (1962) 565.
11 L. Markó, G. Bor and E. Klumpp, *Chem. Ind. (London)*, (1963) 1491.
12 W. Hieber and J. Gruber, *Z. Anorg. Allgem. Chem.*, 296 (1958) 91.
13 P. Szabó, L. Markó and G. Bor, *Chem. Tech. (Berlin)*, 13 (1961) 549.