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REACTIONS OF BIS(THIOCARBONYL)DISULFANE WITH SOME METAL CARBONYLS. PREPARATION OF SULFIDES OF IRON AND MANGANESE CARBONYLS

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Summary

On treatment with some transition metal carbonyls, bis(thiocarbonyl)disulfane decomposes and acts as a sulfurizing agent. The reaction provides a novel method of preparing the known complex, triiron enneacarbonyl disulfide, and has led to preparation of the new compound, dimanganese octacarbonyl disulfide. The mass spectrum of the iron complex is discussed and the structure of the manganese complex assessed on the basis of its infrared spectrum in the C—O stretching region.

Introduction

Triiron enneacarbonyl disulfide has been prepared before in small yields by the reaction between $HFe(CO)_4^-$ and sulfite ion [1], and by treatment of $Fe_3(CO)_{12}$ with cyclohexene sulfide or 3-chloropropylene sulfide [2]. More recently it has been obtained as a by-product of the reaction between various thiobenzophenones and diiron enneacarbonyl [3]. X-ray diffraction studies have shown that $Fe_3(CO)_9S_2$ possesses crystallographic C_sm symmetry, and that like $Fe_3(CO)_9Se_2$ [1], it contains a new type of a seven-coordinated metal [4, 5]. No unambiguous evidence is found in literature for the existence of a manganese carbonyl sulfide, although in a very recent publication [6] it is stated that a polymeric complex $[SMn(CO)_3]_n$ is formed as a by-product of the reaction between various thiobenzophenones and dimanganese decacarbonyl.

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Results and discussion

Bis(fluorocarbonyl)disulfane can be prepared by prolonged shaking of FC(O)SCl [7] with mercury or by irradiating FC(O)SCl in an excess of carbon disulfide [8]. As part of a detailed study of properties of this compound, to we examined its reactions with some transition metal carbonyls. No reaction was observed when the disulfane was stirred at, or slightly above, room temperature with chromium, molybdenum, or tungsten carbonyls. However, at more elevated temperatures or under UV-irradiation, decomposition took place with vigorous gas evolution. The residue was found to contain elemental sulfur as well as unidentified solids containing the transition metal. In addition to relatively copious quantities of carbon monoxide, the evolved gases also contained carbonyl difluoride and carbonyl sulfide, as identified by their IR spectra. The results were quite different when the disulfane was treated in an autoclave with iron pentacarbonyl or dimanganese decacarbonyl in benzene at 74-80°. On purification of the reaction products and recrystallization from pentane and carbon disulfide, triiron enneacarbonyl disulfide and dimanganese octacarbonyl disulfide were obtained in good yield. The iron complex was in the form of dark, pink-red, shining, needle shaped crystals (m.p. 114°); these properties and its infrared spectrum are identical with those reported previously [4, 9]. A ^{19}F NMR spectrum in benzene hexafluoride solution was identical with that of the pure solvent with no broadening or any chemical shifts, indicating that the compound is diamagnetic. In view of the controversy about the identity of this iron complex [9], it was subjected to electron impact. The fragmentation pattern was found to be fully consistent with its X-ray structure [5], i.e., it showed, in addition to the molecular ion peak a successive loss of the nine carbonyls. The residual $S_2Fe_3^+$ ion constitutes the most abundant peak in the mass spectrum. This degradation to the unusually stable S_2Fe_3 entity can be compared with the degradation of $Fe_3(CO)_{12}$, in which stepwise loss of carbonyl groups as far as $Fe_3(CO)_3^+$ is observed [10]. However, there is an important difference in that further degradation of $Fe_3(CO)_{12}$ beyond the $Fe_3(CO)_4^+$ stage takes place by rupture of iron—iron bonds producing fragments of the general formula $Fe_{1-2}(CO)_{1-4}$ [10]. The bonding [11] in the iron-atom grouping seems to be considerably strengthened by the inclusion of the two sulfur atoms. The fragmentation of $Fe_3(CO)_9S_2$ may thus be represented by the following scheme:

$$Fe_3(CO)_9S_2 \rightarrow Fe_3(CO)_9S_2^+ \rightarrow Fe_3(CO)_nS_2^+ \ (n = 8\text{-}0)$$

Dimanganese octacarbonyl disulfide was obtained in the form of minute golden-yellow crystals. Its infrared spectrum in the carbonyl stretching region shows four bands, of which that on the high energy side is relatively weak. Since the frequencies all lie in the 2100—1900 cm^{-1} range, it is safe to assume that the compound is a dimer with no bridging carbonyl groups. This assumption is in accord with observations made on tetracarbonyl halide dimers of manganese and its congeners, technetium and rhenium [12]. In view of the expected octahedral local symmetry around each metal atom, and the tendency of the sulfur atom to act as a bridging atom, it is suggested that this molecule $[Mn(CO)_4S]_2$ has a structure similar the the tetracarbonyl halide dimers of manganese, i.e., of D_{2h} symmetry [17]. A corroborating factor worth mentioning is that this complex was found by ^{19}F NMR measurements to be diamagnetic.

Experimental

All experiments were performed under oxygen-free nitrogen or pure argon. IR spectra were recorded with cyclohexane solutions on a Perkin—Elmer Model 125 grating spectrophotometer. The ^{19}F NMR spectra were performed on a Bruker HX-60/5 Spectrometer. Mass spectrometric measurements were taken on a CH-5 Varian-MAT mass spectrometer at 70 eV electron energies, with an emission of 100 A and an HTE 150° inlet system.

Prepration of triiron enneacarbonyl disulfide

2.0 g (10.2 mmol) of iron pentacarbonyl and 20 ml benzene were placed in a 300 ml autoclave that had been flushed with argon. The sealed autoclave was cooled with liquid nitrogen and after evacuation 2.8 g (17.7 mmol) bis(fluorocarbonyl)disulfane were added via a vacuum system. The autoclave was then kept for 14 h at 78-80° under constant stirring. After cooling to room temperature the mixture was filtered and the solvent of the dark pink-red filtrate was evaporated off under a constant flow of argon. The dark pink-red solid was recrystallized four times from a pentane/carbon disulfide mixture, giving 0.44 g (26.7% yield) of dark pink-red, needle shaped crystals of triiron enneacarbonyl disulfide [found: C, 22.42; Fe, 34.77; S, 13.32. *M* (by mass spec.), 484. $C_9Fe_3O_9S_2$ calcd.: C, 22.34; Fe, 34.62; S, 13.26%; *M*, 484].

Preparation of dimanganese octacarbonyl disulfide

The same procedure as above was followed, using 0.5 g (1.28 mmol) dimanganese decacarbonyl, 18 ml benzene and 1.4 g (8.85 mmol) bis(fluorocarbonyl)disulfane and using a temperature of 75-76°. The recrystallized product which was unstable in the air, was 0.22 g (43.1% yield) of light, golden-yellow, dimanganese octacarbonyl disulfide [found: C, 24.27; Mn, 27.58; S, 16.32; *M* (by mass spec.), 398. $C_8Mn_2O_8S_2$ calcd.: C, 24.14; Mn, 27.61; S, 16.11%; *M*, 398], m.p. 128°. This compound is soluble in the common organic solvents. IR (cm^{-1}, in cyclohexane): ν(C≡O) 2098 w, 2068 vs, 2015 s, 1991 m; other 745 vs, 725 m, 635 (sh), 625 w.

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