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# REACTIVITY OF METAL–METAL BONDS
# VII. THE REACTION OF SULFUR DIOXIDE WITH COMPOUNDS CONTAINING Si–Fe, Ge–Fe, AND Sn–Fe BONDS

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## SUMMARY

Sulfur dioxide reacts readily with $(CH_3)_3M$–$Fe(CO)_2(\pi\text{-}C_5H_5)$ where $M = Ge$ or Sn, but surprisingly does not react even at 76° with the species where $M = Si$. For both the germanium and tin compounds, cleavage of the M–Fe bond occurs and there is no evidence for cleavage of $M$–$CH_3$ bonds. The germanium containing product is formulated as $(CH_3)_3Ge$–$S(O)_2$–$Fe(CO)_2(\pi\text{-}C_5H_5)$ while the tin product is apparently a polymer containing Sn–O–S(O)–Fe units.

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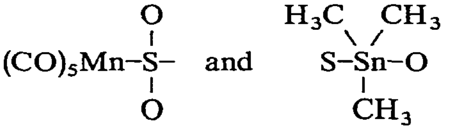
The insertion of sulfur dioxide into metal–carbon bonds has been studied extensively by Wojcicki and coworkers[1–5], the products being sulfinates with either oxygen or sulfur bound to the metal. Insertion of sulfur dioxide into the tin–tin and tin–manganese bonds also occurs[6], giving products which contain varying amounts of sulfur dioxide. In the compound $(CH_3)_3SnMn(CO)_5 \cdot 1\frac{1}{2}\,SO_2$, both the groups



$$(CO)_5Mn\text{–}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}\text{–} \quad \text{and} \quad \overset{\displaystyle H_3C\;\;CH_3}{S\text{–}\underset{\displaystyle CH_3}{Sn}\text{–}O}$$

are indicated from spectroscopic data, the evidence also being consistent with metal–metal bond cleavage. However, the insertion of sulfur dioxide into a metal–carbon bond of a metal–metal bonded compound has also been observed. Thus, $(C_6H_5SO_2)_2$-$Sn[Fe(CO)_2\pi\text{-}C_5H_5]_2$, formed[7] from sulfur dioxide and $(CH_3)_2Sn[Fe(CO)_2$-$(\pi\text{-}C_5H_5)]_2$, has been shown[8] to contain C–S(O)–O–Sn units and intact metal–metal bonds. In view of these two possibilities, metal–metal or metal–carbon bond insertion, it was of interest to examine the behavior of the three compounds $(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5)$, where $M = Si$, Ge, or Sn, with sulfur dioxide.

## EXPERIMENTAL

The procedures for the preparation of $(CH_3)_3SiFe(CO)_2(\pi\text{-}C_5H_5)$, $(CH_3)_3$-$GeFe(CO)_2(\pi\text{-}C_5H_5)$, and $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ are described in part VIII of this series[9]. Standard vacuum techniques were employed throughout; other general procedures and instrumentation are described in part VIII[9].

### (*a*). *Sulfur dioxide with (trimethylstannyl)(cyclopentadienyl)iron dicarbonyl*

Sulfur dioxide (5 ml, Matheson, anhydrous) and $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ (0.5 g, 1.5 mmole) were sealed in a Pyrex Carius tube. After being shaken for 5 h the tube was opened and all volatile materials removed. The residue was extracted with dichloromethane which on evaporation gave a brown solid (decomp. 80° with gas evolution), isolated in essentially quantitative yield. (Found: C, 25.45; H, 3.49; S, 10.89. $C_{10}H_{14}FeO_5S_{1.5}Sn$ calcd.: C, 26.3; H, 3.2; S, 11.00%.)

### (*b*). *Sulfur dioxide with (trimethylgermyl)(cyclopentadienyl)iron dicarbonyl*

Sulfur dioxide (5 ml) and $(CH_3)_3GeFe(CO)_2(\pi\text{-}C_5H_5)$ (0.25 g) were allowed to react as in (*a*) above, and the reaction mixture was worked up in the same manner. The residue, after repeated recrystallizations from hexane/dichloromethane mixtures, gave a yellow crystalline solid, m.p. 148–149° (0.20 g, 80% yield), identified as $(CH_3)_3GeSO_2Fe(CO)_2(\pi\text{-}C_5H_5)$. (Found: C, 33.21; H, 3.85; S, 8.75. $C_{10}H_{14}GeFeO_4S$ calcd.: C, 33.48; H, 3.91; S, 8.92%.)

### (*c*). *Sulfur dioxide with (trimethylsilyl)(cyclopentadienyl)iron dicarbonyl*

(*i*). Sulfur dioxide (5 ml) and $(CH_3)_3SiFe(CO)_2(\pi\text{-}C_5H_5)$ (0.50 g) were treated as in (*a*) above. After removal of all volatile material, the residue was found to contain only unchanged silicon–iron compound.

(*ii*). Sulfur dioxide (5 ml) and $(CH_3)_3SiFe(CO)_2(\pi\text{-}C_5H_5)$ (0.50 g) were sealed in a Pyrex Carius tube and heated at 76° for 24 h. Carbon monoxide (0.9 mmole) was formed. Extraction of the remaining involatile material with organic solvents gave a black tar from which no identifiable product could be obtained, nor did the infrared spectrum show any peaks characteristic of the original silicon–iron compound. A black solid insoluble in common organic solvents remained.

## DISCUSSION

The reaction of $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ with liquid sulfur dioxide gave a glassy product of composition $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)\cdot 1\frac{1}{2}\,SO_2$, analogous[6] to the compound $(CH_3)_3SnMn(CO)_5\cdot 1\frac{1}{2}\,SO_2$. These products are not simply M–S(O)$_2$–M′ or M–(SO$_2$)$_2$–M′ compounds. Spectroscopically, the Sn–Mn and Sn–Fe products are very similar. The compound $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)\cdot 1\frac{1}{2}\,SO_2$ showed in its infrared spectrum, broad intense SO stretching absorptions at 950–990 $cm^{-1}$, although weaker, broad absorptions were also observed in the region of 1150 $cm^{-1}$. The tin–methyl stretching mode, observed at approximately 500 $cm^{-1}$ in the parent tin–iron compound is no longer observed and probably constitutes a part of the intense absorption at approximately 550 $cm^{-1}$. Similarly, the $^{119}$Sn–C–H coupling constant increases from 48 Hz in $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ to 64 Hz in the insertion product. These spectroscopic data are similar to those observed[6] for $(CH_3)_3SnMn(CO)_5\cdot 1\frac{1}{2}\,SO_2$ and also generally for the compounds[10] $(CH_3)_3SnSO_2R$, and are consistent with approximately planar trimethyltin groups and with a lowering of the SO stretching frequencies due to intermolecular bonding. Unlike the reaction of $(C_6H_5)_2$-

TABLE 1

INFRARED ABSORPTION FREQUENCIES FOR SULFUR DIOXIDE PRODUCTS

s=strong; m=medium; w=weak; v=very; br=broad; sh=shoulder

| Assignment | $(CH_3)_3GeSO_2Fe(CO)_2(\pi\text{-}C_5H_5)$ | $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)\cdot 1\frac{1}{2}SO_2$ |
|---|---|---|
| CHstr. $CH_3$ | 3120 w | 3110 vw |
| | 2990 w | 2960 vw |
| | 2920 w | 2900 vw |
| CO stretch | 2060 vs | 2050 vs |
| | 2000 vs | 2000 vs |
| C–H def. of $C_5H_5$ | 1430 w | 1425 w |
| Asymm. def. $CH_3$ | 1420 w | |
| S=O asym. str. | 1205 vs | 1220 m |
| | | 1150 m, sh |
| | | 1100 s |
| S=O sym. str. | 1075 vs | |
| Ring def. | 850 m | 840 m |
| Ge–$CH_3$ rock | 790 vs | |
| Sn–$CH_3$ rock | | 780 vs |
| | 650 m | 640 m |
| | 620 vs | 615 vs |
| | | 600 vs |
| Ge–C asym. str. | 585 m | |
| Fe–CO def. | 570 vs | 565 vs |
| Sn–C str. | | 550 vs |
| Ge–C sym. str. | 540 m | |
| | 500 w | 490 w |
| Fe–C str. | 440 vw | 440 w |

$Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ with sulfur dioxide, metal–metal bond cleavage is indicated. The infrared spectrum is consistent with the presence of Sn–O–S(O)–Fe units, and the mode of attachment of the additional sulfur dioxide may well lead to polymerization through intermolecular oxygen–tin bonding. The readiness of tin to adopt penta-coordination is consistent with such polymerization.

The fact that sulfur dioxide inserts in the metal–carbon bond of $(C_6H_5)_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$, but into the metal–metal bond of $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ may not be merely a result of differing metal–carbon bond strengths; it may reflect changes in both the tin–carbon and the tin–iron bonds. Thus, although the compounds are not those used in the present study, the Sn–Fe bond length[11] in $(C_6H_5)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ is 2.53 Å but in $Cl_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ is 2.49 Å. Additionally, in the latter compound[12] the Sn–Cl bond lengths are greater than in dimethyltin dichloride. Changes in the distribution of the bonding orbitals of tin may thus weaken the Sn–C bond or strengthen the Sn–Fe bond of $(C_6H_5)_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ relative to $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$.

(Trimethylgermyl)(cyclopentadienyl)iron dicarbonyl with sulfur dioxide gave a yellow, crystalline 1/1 product. In the proton NMR spectrum, this compound shows only two singlets, one at $\tau$ 9.5 due to the $CH_3$ protons and one at $\tau$ 5.0 due to $C_5H_5$, these being only slightly shifted from the corresponding resonances for the parent Ge–Fe compound. Insertion into the $CH_3$–Ge bonds has not, therefore, occurred. In the infrared spectrum, the symmetric and asymmetric S–O stretching frequences are at 1075 and 1205 cm$^{-1}$ respectively indicating[2] that the product is a sulfone with both iron and germanium bound to sulfur. The Ge–C stretching absorptions at 585 (asymmetric) and 540 (symmetric) and the carbonyl vibrations at 2060 and 2000 cm$^{-1}$ are similar to those observed for $(CH_3)_3GeFe(CO)_2(\pi\text{-}C_5H_5)$, although the latter frequencies are about 60 cm$^{-1}$ higher in the sulfur dioxide product.

(Trimethylsilyl)(cyclopentadienyl)iron dicarbonyl did not react with liquid sulfur dioxide, and while reaction occurred at 80°, the product was a black insoluble solid which was not identified.

The basis for this difference in reactivity towards sulfur dioxide of the silicon, germanium, and tin compounds is not readily found, but interestingly it is paralleled, at least in part, by other series of Group IV–transition metal derivatives. While $(CH_3)_3SnMn(CO)_5$ give [6], the compound $(CH_3)_3SnMn(CO)_5 \cdot 1\frac{1}{2}\,SO_2$ $(CH_3)_3SiMn(CO)_5$ does not react[13] at all with sulfur dioxide. Similarly, while $(C_6H_5)_3SnMn(CO)_5$ reacts readily giving $(C_6H_5)_3SnMn(CO)_5 \cdot 1\frac{1}{2}\,SO_2$, the analogous $(C_6H_5)_3GeMn(CO)_5$ does not react[3] with sulfur dioxide under reflux conditions. The relative Group IV–transition metal bond energies must be involved in these differences in reactivity, but apparently need not be the determining factors.

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