On the contrary, in reaction 1 also at high concentrations of the ligand L′, the rates of reaction do not depend on the nature and concentration of L′. As an example, the values of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}), for the reaction of $Re(CO)_4BrP(C_6H_5)_3$ with $L' = P(C_6H_5)_3$ at 60° in CCl_4 are 13.9×10^{-5} ($L' = 0.02\ M$) and 13.8×10^{-5} ($L' = 0.208\ M$). For the analogous reaction with L′ = pyridine in the same experimental condition, the values found are 15.2×10^{-5} ($L' = 0.0188\ M$) and 15.3×10^{-5} ($L' = 0.424\ M$). Similar results are obtained in the case of other examined substrates.

Data in Table III show that the rate constants for reaction 1 decrease with changes in X in the order $Cl > Br > I$. This is the same reactivity order as found for the reactions of the analogous manganese compounds.[8, 9] This has been explained on the basis of the difference in electronegativity of halogen ligands: the more electronegative chlorine causes a lower electron density on rhenium which in turn means less back-donation of d electrons, lower metal–CO bond strength, and therefore faster reaction.

Furthermore the data in Table III indicate a decrease in the rate of reaction 1 with changes in the coordinated ligand L in the order: $\gamma\text{-pic} = \text{py} \gg P(C_6H_5)_3 > P(C_6H_5)_2(C_2H_5) > P(n\text{-}C_4H_9)_3$. It has been reported that the rates of reaction

$$Mn(CO)_4XL + L' \longrightarrow Mn(CO)_3XLL' + CO \qquad (5)$$

were independent of L′ concentration and were decreased by reducing the bulkiness of the coordinated ligand L.[9] Our results for $Re(CO)_4XL$ are in agreement with a similar behavior when the coordinated ligands L are bases with the same donor atom (*i.e.*, $P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $P(n\text{-}C_4H_9)_3$). Conversely, when L is pyridine or substituted pyridine, the rates of reaction 1 are considerably larger. The decreasing first-order rate constant with change in the donor atom of the coordinated L is opposite to that expected on the basis of the decreasing metal–CO bond order in the ground state with increasing π-acceptor properties of the coordinated ligand L. Thus a reason for such behavior ought to be found in a different stabilization imposed by the σ-donor pyridine in comparison to the π-acceptor phosphine upon the coordinately unsaturated complex in the transition state. The same type of reasoning applied to the comparison between the rate constants when $L = P(C_6H_5)_3$ and $P(n\text{-}C_4H_9)_3$ would predict a larger rate for $P(n\text{-}C_4H_9)_3$, which is not the case. However, in this particular case, it should be considered that a steric acceleration by $P(C_6H_5)_3$ probably overrides the electronic effect of $P(C_6H_5)_3$.

TABLE IV
ACTIVATION PARAMETERS FOR REACTION 1 IN CCl_4 SOLUTION

$$Re(CO)_4XL + L' \longrightarrow Re(CO)_3XLL' + CO$$

$Re(CO)_4XL$	L′	ΔH^*, kcal/mole	ΔS^*, eu
$Re(CO)_4Cl(py)$	Pyridine	28	15
$Re(CO)_4Br(py)$	Pyridine	29	14
$Re(CO)_4I(py)$	Pyridine	29	10
$Re(CO)_4ClP(C_6H_5)_3$	$P(C_6H_5)_3$	28	11
$Re(CO)_4BrP(C_6H_5)_3$	$P(C_6H_5)_3$	34	26

Some activation parameters for reaction 1 are given in Table IV.

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CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT,
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Tetra(methylgermanium) Hexasulfide

BY KURT MOEDRITZER

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As evidenced by recent reviews,[1] organogermanium sulfur compounds have received little attention in the past, although corresponding compounds of silicon or tin are quite well known. Examples of organogermanium sulfides of the general formula $(R_3Ge)_2S$ and $(R_2GeS)_3$ have been described previously. However, crystalline species of the corresponding sulfides based on monoalkylgermanium moieties, having the general formula $(RGeS_{1.5})$, do not seem to have been reported, although amorphous aryl derivatives[1] have been described.

Owing to the ready availability of alkylhalogermanes by an improved version[2] of the direct synthesis,[3] the latter are now conveniently accessible so that synthesis of a prototype of the missing low molecular weight sulfide has been undertaken. A method of preparation has been used which was previously applied to the synthesis of analogous monoalkylsilicon sulfides,[4,5] $(RSiS_{1.5})_4$. It is based on the reaction

$$4CH_3GeBr_3 + 6H_2S + 12N(C_2H_5)_3 \longrightarrow (CH_3GeS_{1.5})_4 + 12N(C_2H_5)_3\cdot HBr \qquad (1)$$

The tetra(methylgermanium)hexasulfide thus prepared is a stable, crystalline, high-melting material which, because of its molecular weight and mass spectroscopic cracking pattern, must consist of four $(CH_3GeS_{1.5})$ moieties—probably arranged in a structure of the type I or II.

The "adamantane" skeleton of structure I, which is found in some organic and inorganic compounds,[6] is

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[1] D. Quane and R. S. Bottei, *Chem. Rev.*, **63**, 403 (1963). See also O. H. Johnson, *ibid.*, **48**, 259 (1951).

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[3] E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 1729 (1947).

[4] M. Y. Etienne, *Compt. Rend.*, **235**, 966 (1952).

[5] M. Y. Etienne, *Bull. Soc. Chim. France*, 791 (1953).

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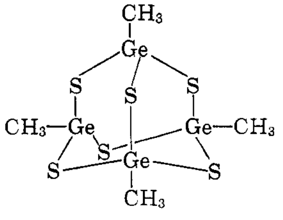

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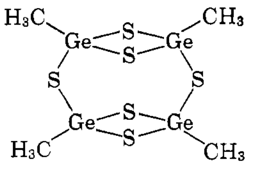

II

thought to be more likely than structure II, which involves strained four-atom germanium–sulfur rings. The single proton nuclear magnetic resonance (nmr) signal observed for solutions of tetra(methylgermanium) hexasulfide is in accord with either I or II. The infrared spectrum is simple. A structure of the type of I has been suggested for the tetra(alkylsilicon) hexasulfide and the tetra(alkylsilicon) hexaselenide[7] on the basis of such spectroscopic data.

ADDED IN PROOF.—A single crystal X-ray study of $(CH_3GeS_{1.5})_4$ as well as of $(CH_3SiS_{1.5})_4$ showed that both compounds are isomorphous and isostructural with a monoclinic space group Cc or C2/c, with the latter more probable. For the space group C2/c the molecule has either a center of symmetry or a twofold axis. Unfortunately this does not permit one to distinguish between I and II. Structure II may have a center of symmetry or a twofold axis while I may have a twofold axis.

Experimental Section

Materials.—Methyltribromogermane was prepared by a modified version of the direct synthesis;[2,3] triethylamine was obtained from Matheson Coleman and Bell, and hydrogen sulfide, from Matheson Co.

Preparation and Characterization.—Methyltribromogermane (22.2 g, 0.068 mole) and triethylamine (20.7 g, 0.204 mole) were dissolved in 0.5 l. of dry benzene in a three-necked flask fitted with a reflux condenser, stirrer, and gas-inlet tube. Hydrogen sulfide was passed over phosphorus pentoxide and bubbled into the solution until no more precipitate was formed. After 1 hr at reflux temperature, the solution was filtered, yielding 37.4 g (0.195 mole) of triethylamine hydrobromide (mp 250°). The resulting clear benzene solution was evaporated to dryness *in vacuo* yielding a slightly yellow solid product, which upon recrystallization from benzene melted at 345–346°; yield, 7.8 g (84%). The product is soluble in benzene and chloroform.

Anal. Calcd for $(CH_3GeS_{1.5})_4$: C, 8.85; H, 2.23; Ge, 53.49; S, 35.43; mol wt, 543. Found: C, 9.04; H, 2.24; Ge, 53.39; S, 35.38; mol wt, 529 (osmometric in chloroform).

The proton nmr spectrum in chloroform consists of a very sharp singlet at −1.316 ppm relative to internal tetramethylsilane. The infrared spectrum (as a KBr pellet) shows absorptions at 1235 (s), 1213 (w), 1035 (w), 870 (sh), 805 (vs), and 755 (w) cm^{-1} and thus resembles quite closely that reported[7] for the analogous silicon compound, $(CH_3SiS_{1.5})_4$. In the fragmentation pattern in the mass spectrometer, the largest fragment was seen at *m/e* 541 with additional predominant ions at *m/e* 491, 479, 417, 405, 343, and 149.

ADDED IN PROOF.—The unit cell data for $(CH_3GeS_{1.5})_4$ are the following (with the corresponding data for $(CH_3SiS_{1.5})_4$ listed in parentheses): $a = 9.40$ (9.38), $b = 16.72$ (16.51), $c = 10.57$ (10.58) A; $\beta = 108°$ (107.2°). Assuming four molecules of the tetramer in the unit cell, the molecular weight was found to be 531 (calcd 543) for the germanium compound and 368 (calcd 365) for the silicon compound.

Acknowledgment.—The author wishes to thank Dr. J. J. Daly of Monsanto Research S.A. for the X-ray structure study and the Physical Sciences Center of Monsanto Co. for the analytical and mass data.

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CONTRIBUTION NO. 1244 FROM THE CENTRAL RESEARCH
DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE
NEMOURS AND COMPANY, WILMINGTON, DELAWARE

Mössbauer Effect Studies of $(CH_3)_4Sn_3Fe_4(CO)_{16}$ and $(CH_3)_4Sn_2Fe_2(CO)_8$

BY M. THOMAS JONES[1]

Received September 2, 1966

Mössbauer effect (ME) studies of $(CH_3)_4Sn_3Fe_4(CO)_{16}$ and $(CH_3)_4Sn_2Fe_2(CO)_8$ were performed to gain a better understanding of the bonding and electronic structure of these compounds and to demonstrate the chemical applications of the Mössbauer effect. An additional reason for initiating the study is that iron and tin, two ME nuclei, are rarely found in the same compound. The two primary pieces of data, of most interest to chemists, which one obtains from a ME experiment[2] are the isomer shift (δ) and the quadrupolar splitting (Δ).

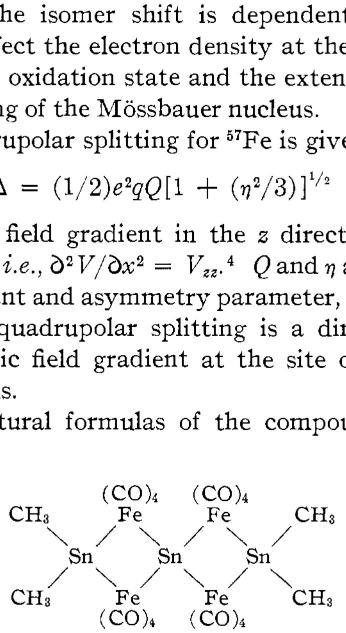
The isomer shift is proportional to $|\psi_s(0)|_A{}^2 - |\psi_s(0)|_S{}^2$, where $|\psi_s(0)|^2$ is the electron density at the Mössbauer nucleus, A denotes the absorber, and S the source. Therefore, the isomer shift is dependent upon such factors as affect the electron density at the nucleus, for example, the oxidation state and the extent of covalent and π bonding of the Mössbauer nucleus.

The quadrupolar splitting for ^{57}Fe is given by[3]

$$\Delta = (1/2)e^2qQ[1 + (\eta^2/3)]^{1/2}$$

The electric field gradient in the z direction is represented by eq, *i.e.*, $\partial^2V/\partial x^2 = V_{zz}$.[4] Q and η are the quadrupole moment and asymmetry parameter, respectively. Hence, the quadrupolar splitting is a direct measure of the electric field gradient at the site of the Mössbauer nucleus.

The structural formulas of the compounds studied are



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[1] Department of Chemistry, St. Louis University, St. Louis, Mo.

[2] One also observes magnetic hyperfine splitting in magnetically ordered materials. However, that will not be of concern with respect to the compounds studied here.

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[4] Strictly, for the electric field gradient in the z direction, $eq = -V_{zz}$. For convenience many people redefine $eq = V_{zz}$ as has been done here. See M. H. Cohen and F. Reif, *Solid State Phys.*, **5**, 321 (1957).