The Electronic Effect of XMe_3 and CH_2XMe_3 (X = Si, Ge, Sn, or Pb) Substituents in Organometallic Sulphides. A Kinetic and Photoelectron Spectroscopic Study

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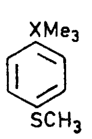
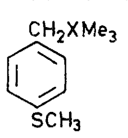
For organometallic sulphides p-$Me_3XC_6H_4SMe$ (I), p-$Me_3XCH_2C_6H_4SMe$ (II), and $PhSCH_2XMe_3$ (III) (X = Si, Ge, Sn, or Pb) the oxidation rates with perbenzoic acid have been measured spectrophotometrically at 25° and compared with the ionization energies obtained by u.v. photoelectron spectroscopy measurements. From the results obtained for sulphides (I), $+I$, $(p \longrightarrow d)_\pi$, and hyperconjugative contributions almost cancel out; for series (II) and (III) however the electron-releasing character of the CH_2XMe_3 group confirms the importance of *C*-metal hyperconjugation. Solvent effects on the oxidation rates of the title compounds have also been studied and are discussed in detail.

THE chemistry of the C–X bond (X = Si, Ge, Sn, and Pb) has received[1] a great deal of attention. However, despite the large number of investigations, considerable interest continues in the problem of metallo-substituent effects. In this paper we present kinetic data for the oxidation of sulphides (I)—(III) to the corresponding sulphoxides and the related ionisation energies determined by means of photoelectron spectroscopy. The aim of this work is to acquire further information on the substituent effects of XMe_3 and CH_2XMe_3 groups from consideration of an electrophilic substitution whose mechanism does not include charge separation in the transition state and to compare the data obtained for this reaction with the ionization potentials.


(I)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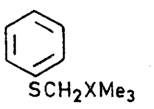
(III)

X = Si, Ge, Sn, or Pb

TABLE 1

Second-order rate constants (k_2) for the oxidation of sulphides (I)—(III) and substituted thioanisoles with perbenzoic acid at 25° in various solvents

	p-$Me_3XC_6H_4SMe$		p-$Me_3XCH_2C_6H_4SMe$		$C_6H_5SCH_2XMe_3$		XC_6H_4SMe	
Solvent	X	k_2/l $mol^{-1}s^{-1}$	X	k_2/l $mol^{-1}s^{-1}$	X	k_2/l $mol^{-1}s^{-1}$	X	k_2/l $mol^{-1}s^{-1}$
Carbon tetrachloride	C	114.8					p-OMe	190.5
	Si	81.8	Si	138.1	Si	174.6	p-Me	147.6
	Ge	86.9					H	77.6
	Sn	93.3	Sn	160.3	Sn	592.3	p-Br	35.2
	Pb	107.2					p-NO_2	5.98
Methylene chloride	Si	204.7	Si	363.1	Si	195.4		
	Ge	208.9						
	Sn	186.9	Sn	595.7	Sn	835.8		
Dioxan	Si	15.4	Si	17.9	Si	25.3	p-OMe	40.5
	Ge	14.4					p-Me	28.5
	Sn	14.7	Sn	52.3	Sn	110	H	14.1
							p-Br	8.03
							m-NO_2	1.64

RESULTS AND DISCUSSION

The oxidation of sulphides (I)—(III) to the corresponding sulphoxides with perbenzoic acid (PBA) has been studied kinetically in different solvents. The results are shown in Table 1 as second-order rate constants, k_2, together with those for the corresponding thioanisoles.

To detect the contributions of inductive, $(p \longrightarrow d)_\pi$, and hyperconjugative effects exerted by XMe_3 and CH_2XMe_3 in sulphides (I)—(III), we have also determined the ionization energies (IE) of the sulphur n_π orbital. Photoelectron spectroscopy data are collected in Table 2.

For sulphides (I), the kinetic results in CCl_4 as solvent indicate that the reaction rate is fairly insensitive to the nature of the group IVB element; moreover by comparison with the carbon derivative (X = C), these organometallic sulphides exhibit a small decrease in reactivity but the oxidation rate is slightly faster than for thioanisole. Insertion of a methylene group between the XMe_3 substituent and the phenyl group in sulphides (II) modifies the reactivity. From Table 1 these compounds appear in fact to be more reactive towards PBA than the analogues (I); furthermore comparison between the tin and silicon derivatives shows that the oxidation rate lies in the sequence Sn > Si on changing the metal.

From the data in Table 1 the points for the five common substituents define a straight line * of slope ρ -1.44 and the use of this slope provides an estimate of

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* Based on σ values reported by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[1] C. Eaborn, ' Organosilicon Compounds,' Butterworths, London, 1960, p. 91; V. Băzant, ' Organosilicon Compounds,' Academic Press, New York, 1965; J. Chatt and A. A. Williams, *J. Chem. Soc.*, 1954, 4403; A. G. McDiarmid, ' Organometallic Compounds of the Group IV Elements,' Dekker, New York, 1968, vol. 1, parts I and II.

the substituent constants for the XMe_3 and CH_2XMe_3 groups in the oxidation reaction. The XMe_3 substituents (X = Si, Ge, Sn, and Pb) exhibit small σ values ranging between −0.02 and −0.08. These figures are in satisfactory agreement with previous findings based on dissociation constants[2] and spectroscopic studies[3] and indicate in the reaction studied an almost negligible overall electron-releasing effect in the Group IVB series.

TABLE 2

Ionization energy (IE) data (eV) for sulphides (I)—(III) and substituted thioanisoles

Compound	X	IE
p-$Me_3XC_6H_4SMe$	C	7.83
	Si	7.93
	Ge	7.90
	Sn	7.87
	Pb	8.02
p-$Me_3XCH_2C_6H_4SMe$	Si	7.72
	Sn	7.70
$PhSCH_2XMe_3$	Si	7.81
	Sn	7.74
p-XC_6H_4SMe	p-OMe	7.8 [a]
	p-Me	7.9 [a]
	H	8.07 [a]
	p-Br	8.17
	p-NO_2	8.59 [a]

[a] See ref. 11.

On the other hand the σ derived values for CH_2SiMe_3 and CH_2SnMe_3 in the oxidation study are −0.16 and −0.20 respectively, near that for the p-CH_3 group, thus confirming the electron-releasing character of these substituents.

If one accepts that such electron donation is mainly hyperconjugative in origin,[4] the overall effect exerted by CH_2XMe_3 groups in the oxidation reaction is relatively small. This is however consistent with the fact that the reaction centre is far away from the substituent and that C–X hyperconjugation stabilizes carbonium ions,[5] whereas the accepted mechanism[6] for the oxidation with PBA precludes charge separation in the transition state.

Solvent effects on the reaction rates are important. For all the sulphides studied, the most evident feature is the drop in the rate constants on passing from chlorinated to basic non-protic solvents.[6] Moreover within compounds (I), no appreciable changes occur on changing the solvent but for series (II) the $k_{2\mathrm{Sn}}$: $k_{2\mathrm{Si}}$ ratio varies from 1.2 in CCl_4 to 1.6 in CH_2Cl_2 to 2.9 in dioxan. Since the ρ value is substantially the same in CCl_4 and in dioxan as shown by the similarity of the trends derived from thioanisoles in these two solvents (Table 1), the dependence of the reaction rates on the nature of the solvent for (II) can be ascribed with confidence to specific solvent–substrate interactions. A reasonable assumption which accounts for the rate ratios is that dioxan can co-ordinate with the metal centre: this can promote[7] polarization of the CH_2^+-X^- bond in series (II) to an extent which is related to the ability of the metal to co-ordinate (Sn > Si),[8] thus increasing the hyperconjugative contribution. Comparison between the oxidation rates and ionization potentials exhibits several discrepancies but this is not surprising since no simple relationship exists between reactivity data and IE measurements because in the oxidation process all occupied MOs which are non-nodal at the sulphur atom are involved and linear correlation would not be anticipated.[9] From previous studies the total electronic effect of the XMe_3 groups on the energy of the highest occupied molecular orbital (HOMO) in the $PhXMe_3$ derivatives has been shown[10] to be much the same as a consequence of the balance of inductive, hyperconjugative, and $(p \longrightarrow d)_\pi$ effects (the IEs are 9.1, 8.98, 8.83, and 8.82 for X = Si, Ge, Sn, and Pb respectively). On the other hand, the HOMO in thioanisole and in its *para*-derivatives is formed by the non-bonding combination of the sulphur 3p and the appropriate ring and substituent π orbitals with the prevailing contribution from the sulphur lone pair.[11] For these reasons, the energy of the π-MO mainly localized on the sulphur atom in the p-$CH_3SC_6H_4XMe_3$ compounds, is expected to change only a little along the series and with respect to the thioanisole value.

Concerning series (II) the reduction of the first IE with respect to the above series (I) (0.2 eV) is much smaller than that observed between corresponding compounds in $PhXMe_3$ and $PhCH_2XMe_3$ series (0.7 eV).[10] Furthermore no sizeable differences are detected for the p-$CH_3SC_6H_4CH_2XMe_3$ derivatives on changing X (Table 2). These findings are easily explained by considering that the insertion of a methylene group between the ring and the XMe_3 group, reducing the $(p \longrightarrow d)_\pi$ contribution, causes an increase of the energy of the ring π orbital (*i.e.* a reduction of its IE) and a larger interaction with the sulphur lone pair; however since the π-MO is mainly localized on sulphur this interaction will give rise to relatively small effects.

In compounds (III) the oxidation rates (Table 1) still reflect the large availability of the non-bonding electrons of sulphur. Owing to the ease of cleavage of the

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[2] J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Amer. Chem. Soc.*, 1949, **71**, 2923; R. A. Benseker and H. R. Krysiak, *ibid.*, 1953, **75**, 2421.

[3] J. C. Maire and J. M. Angelelli, *Bull. Soc. chim. France*, 1969, 1311.

[4] H. Berwin, *J.C.S. Chem. Comm.*, 1972, 237; A. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometallic Chem.*, 1969, **20**, 49; A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *ibid.*, 1970, **21**, 91; W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 7476; T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, 1971, **93**, 5715; C. G. Pitt, *J. Organometallic Chem.*, 1973, **61**, 49; N. C. Cutress, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *ibid.*, 1972, **43**, 131.

[5] C. Eaborn, *J.C.S. Chem. Comm.*, 1972, 1255, and references therein.

[6] R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, 1970, **35**, 740.

[7] W. Adcock, S. Q. A. Rizvi, W. Kitching, and A. J. Smith, *J. Amer. Chem. Soc.*, 1972, **94**, 369; G. Pirazzini, R. Danieli, A. Ricci, and C. A. Boicelli, *J.C.S. Perkin II*, 1974, 853 and references therein.

[8] R. C. Poller, *J. Organometallic Chem.*, 1965, **3**, 321; M. Gielen and N. Sprecher, *Organometallic Chem. Rev.*, 1966, **1**, 455.

[9] M. Yanez, O. Mo', and J. I. Fernandez-Alonso, *Tetrahedron*, 1975, **31**, 245 and references therein.

[10] G. Distefano, S. Pignataro, A. Ricci, F. P. Colonna, and D. Pietropaolo, *Ann. Chim. (Italy)*, 1974, **64**, 153.

[11] G. Distefano, F. Bernardi, A. Mangini, S. Pignataro, and G. Spunta, *J. Electron. Spectroscopy*, in the press.

sulphur–metal bond by electrophiles, no data are available for sulphur oxidation in the $PhSXMe_3$ compounds. However, comparison between the IE values shows a significant reduction of 0.8 eV in the IEs on going from the $PhSXMe_3$[10] to the $PhSCH_2XMe_3$ (Table 2) compounds. Even if a reduction of the $(p \longrightarrow d)_\pi$ contribution is likely to be mainly responsible for such decrease, a variation of the hyperconjugative interaction cannot be completely dismissed. The results of the oxidation studies indicate (Table 1) the electron-releasing order $Me_3SnCH_2 > Me_3SiCH_2$ and the IE data show the same trend but the differences are just outside the experimental uncertainty. These findings are reasonably consistent with an increased hyperconjugative contribution for the heavier metal. Some difficulty arises in the comparison between the oxidation rates and the IE data for compounds (III). The ionization energies of these compounds are in fact near to those reported for series (II) but the oxidation rates are generally higher. A plausible interpretation for this inconsistency is that sulphur is much more sensitive than in series (II) to the increase of hyperconjugative interactions in the transition state when the substituents are directly bonded to it.

TABLE 3

Analytical data and physical properties of p-XC_6H_4SOMe

X	B.p. (°C)[a] [p/mmHg]	Yield (%)	Found (%) C	Found (%) H	Found (%) S	Required (%) C	Required (%) H	Required (%) S
Me_3Si[b]	120[0.1]	97	56.8	7.4	15.45	56.55	7.6	15.1
Me_3Ge	132[0.5]	90	46.75	5.95	12.4	46.75	6.3	12.5
Me_3Sn	138[0.1]	90	39.85	5.4	10.35	39.65	5.3	10.6
Me_3Pb	135[0.4]	85	30.95	4.3	8.3	30.7	4.1	8.2
Me_3SiCH_2	122[0.2]	95	58.15	7.95	14.3	58.35	8.0	14.15
Me_3SnCH_2	118[0.1]	80	41.95	5.7	9.95	41.65	5.75	10.15

[a] Uncorrected. [b] A. C. Boicelli, R. Danieli, A. Mangini, G. Pirazzini, and A. Ricci, *J.C.S. Perkin II*, 1974, 1343.

EXPERIMENTAL

Materials.—Reagent grade carbon tetrachloride, methylene chloride, and 1,4-dioxan, purified according to standard procedures,[12] and conductivity water were used for the kinetic experiments. Perbenzoic acid[13] was crystallized from light petroleum. Commercially available 4-bromothioanisole (Fluka) was crystallized from ethanol before use. 4-Methoxy-,[14] 4-methyl-,[15] and 4-nitro-thioanisoles,[16] were synthesized by literature methods. The general procedure previously used[17] for 4-trimethylsilylthioanisole was employed for the synthesis of compounds (I).

4-*Trimethylgermylthioanisole.*—The Grignard reagent obtained from the reaction of 4-bromothioanisole (3.2 g, 14 mmol) with Mg turnings (0.37 g, 15 mmol) in dry ether (30 ml) was treated with trimethylgermyl bromide (3 g, 15 mmol) and the mixture was refluxed overnight. Hydrolysis with aqueous ammonium chloride and work-up of the reaction mixture gave 4-*trimethylgermylthioanisole* (29%) b.p. 88—90° at 0.3 mmHg (Found: C, 49.8; H, 6.9. $C_{10}H_{16}GeS$ requires C, 49.85; H, 6.7%).

4-*Trimethylstannylthioanisole.*—This was obtained in good yield (70%) as described above by reacting the Grignard reagent from 4-bromothioanisole in ether with trimethyltin chloride, b.p. 104° at 0.3 mmHg (Found: C, 41.7; H, 5.7. $C_{10}H_{16}SSn$ requires C, 41.85; H, 5.6%).

4-*Trimethyl-leadthioanisole.*—The Grignard reagent from 4-bromothioanisole (1.8 g, 9 mmol) in ether (50 ml) was treated with trimethyl-lead chloride (2.6 g, 9 mmol) in dry tetrahydrofuran and the mixture was refluxed for two days. The usual work-up gave 4-*trimethyl-leadthioanisole* (22%), b.p. 108° at 0.4 mmHg (Found: C, 32.65; H, 4.55. $C_{10}H_{16}PbS$ requires C,32.0; H, 4.3%).

For sulphides (II) 4-*methylthiobenzyltrimethylsilane* was prepared in the following way. The Grignard reagent obtained from magnesium (0.9 g, 38 mmol) and 4-bromobenzyltrimethylsilane[18] in dry ether were allowed to react with dimethyl disulphide (3.2 g, 35 mmol) in dry ether and the mixture was refluxed overnight. After hydrolysis with saturated ammonium chloride solution and work up the residual oil was distilled through a 20 cm Vigreux column. Careful fractionation yielded 4-*methylthiobenzyltrimethylsilane* (32%), b.p. 118° at 0.1 mmHg (Found: C, 62.6; H, 8.45. $C_{11}H_{18}SSi$ requires C, 62.8; H, 8.6%).

4-*Methylthiobenzyltrimethyltin.*—To a solution of the lithium salt[19] prepared from trimethyltin chloride (4 g, 50 mmol) and lithium (1.4 g, 200 mmol) in dry tetrahydrofuran (80 ml), p-bromomethylthioanisole (3 g, 15 mmol) in dry tetrahydrofuran (20 ml) was added dropwise. The mixture was refluxed overnight, the solvent evaporated, and after addition of ether, the residue was hydrolysed with saturated ammonium chloride solution. Evaporation of the ether layer gave a residue which was extracted with light petroleum. Evaporation of the solvent and vacuum distillation gave 4-*methylthiobenzyltrimethyltin* (25%), b.p. 91° at 0.1 mmHg (Found: C, 44.2; H, 6.2. $C_{11}H_{18}SSn$ requires C, 43.9; H, 6.0%).

Trimethylsilylmethyl Phenyl Sulphide.—This was prepared by adding to a solution of thiophenol (0.69 g, 6.2 mmol) and triethylamine (0.63 g, 6.2 mmol) in dry benzene (20 ml), a solution of bromomethyltrimethylsilane[20] (1.1 g, 6.5 mmol) in benzene (10 ml). The reaction mixture was refluxed during 3 h, filtered, and the solvent evaporated. Vacuum distillation of the residual oil gave *trimethylsilylmethyl phenyl sulphide* (45%), b.p. 134° at 20 mmHg (Found: C, 61.7; H, 8.25. $C_{10}H_{16}SSi$ requires C, 61.15; H, 8.2%).

Trimethylstannylmethyl Phenyl Sulphide.—This was pre-

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[12] A. Weissberger, 'Technique of Organic Chemistry,' Interscience, New York, 1967, vol. 17.

[13] L. S. Silbert, E. Siegel, and D. Swern, *Org. Synth.*, 1963, **43**, 93; *J. Org. Chem.*, 1962, **27**, 1336.

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[16] Brand and Kranz, *J. prakt. Chem.*, 1927, **115**, 143.

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[18] R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Chem. Soc.*, 1963, 2342.

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pared by a similar technique to that above by reacting thiophenol and triethylamine in dry benzene, with a solution of chloromethyltrimethyltin [21] in anhydrous benzene. The usual work-up gave *trimethylstannylmethyl phenyl sulphide* (39%), b.p. 87° at 0.3 mmHg (Found: C, 41.5; H, 5.4. $C_{10}H_{16}SSn$ requires C, 41.85; H, 5.6%).

Oxidation Products.—For series (I) and (II) these were obtained by oxidation of the parent sulphides with the stoicheiometric amount of *m*-chloroperbenzoic acid in chloroform at 0°. After washing with aqueous sodium hydrogen carbonate, chloroform was evaporated and the residual oil distilled under high vacuum to give the corresponding sulphoxides. The physical properties and yields of these products are in Table 3. For series (III), there was difficulty in obtaining pure sulphoxides owing to ready hydrolysis in the aqueous work-up and thermal rearrangement (limited to the Si compound) during distillation. However for $PhSOCH_2SiMe_3$ the n.m.r. and i.r. spectra of the oxidation mixture were as previously [22] described. Also the oxidation product for the tin-containing sulphide was identified spectroscopically, τ (CCl_4) 9.43 (9 H, s, Me_3Sn) and 7.45 (2 H, s); $\nu_{max.}$ (neat) 961 cm^{-1} ($S \longrightarrow O$).

Kinetic Measurements.—Stock solutions of perbenzoic acid (PBA) were prepared by weighing and standardized by titration using the arsenic oxide–iodine method.[23] The kinetic runs were started in a thermostatted 1-cm quartz cell containing a solution of the sulphide (2 ml, $2-9 \times 10^{-5}$M) and PBA solution (1 ml). The reactions were followed by observing the change of the optical density at the suitable wavelength with a Perkin-Elmer 402 spectrophotometer. The same quantity of perbenzoic acid plus solvent (2 ml) were used in the reference cell. Excess of sulphide over PBA was used in all cases and the second-order rate constant in Table 1 are averages of three or more independent runs. The experimental error was *ca.* ± 2%.

Spectroscopic Measurements.—The ionization energies (I.E.) were obtained by means of a Perkin-Elmer PS18 photoelectron spectrometer. The spectra were calibrated with reference to the Xe and Ar lines. The estimated experimental error is ±0.05 eV for all compounds except $MeSC_6H_4PbMe_3$ for which the quoted figure (8.02 eV) must be considered an upper limit owing to the probable presence of decomposition products.

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