The Molecular Structure of Germyl Monothioacetate in the Gas Phase, determined by Electron Diffraction

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The molecular structure of gaseous germyl monothioacetate has been determined by electron diffraction. The only isomer present has the germyl group bonded to sulphur; the non-bonded Ge · · · O distance is substantially less than the sum of van der Waals radii for germanium and oxygen. Principal bond lengths and angles (r_a) are: r(Ge–S) 223.3(4), r(C–S) 176.5(7), r(C=O) 122.4(8), and r(C–C) 149.3(10) pm; GeSC 96.7(4), SCO 124.1(10), and CCO 116.4(13)°. The heavy-atom skeleton is almost planar, with the Ge–S and C=O bonds arranged *cis* to one another.

The molecular structures of silyl formate [1] and silyl acetate [2] in the gas phase have recently been determined, and in each case the heavy-atom skeleton is planar, with the Si–O and C=O bonds mutually *cis*. This arrangement is associated with an unusually short intramolecular Si · · · O distance of about 280 pm, which is considerably less than the van der Waals Si · · · O distance (360 pm). In the solid phase, the structure of silyl acetate is little changed, although there is also an intermolecular Si · · · O contact of 272 pm.

These observations have prompted us to consider the structures of other silyl and germyl esters. In silyl monothioacetate [3] the silyl group is bonded to oxygen, and in the gas phase a planar heavy-atom structure is found, with a short contact between the silicon and the thiocarbonyl sulphur atoms. This structure is maintained in the solid phase, in which there is also a short intermolecular Si · · · S contact. In contrast, the germyl group of germyl monothioacetate is bonded to sulphur.[4] We have regrettably been unable to grow a single crystal of this compound. However, we are able to report the structure of the gas-phase form, which provides an interesting comparison with the gas-phase data for the silyl ester.

Experimental

A sample of germyl monothioacetate was prepared by reaction of monochlorogermane with tributyltin monothioacetate at room temperature, and was purified by fractional distillation and condensation *in vacuo*. Its purity was checked by i.r. spectroscopy and by molecular weight determination.

Electron-diffraction scattering intensities were recorded photographically on Kodak Electron Image plates using the Cornell/Edinburgh diffraction apparatus [5,6] operating at *ca.* 43 kV. During exposures the nozzle and sample were maintained at room temperature. Three plates were obtained at each camera distance (128 and 286 mm), giving data over a range of 20—336 nm^{-1} in the scattering variable, s. Intensity data were obtained in digital form using a computer-controlled Joyce-Loebl Microdensitometer 6 [7] at the S.E.R.C. Laboratory, Daresbury.

All calculations were carried out on an ICL 2972 computer at the Edinburgh Regional Computing Centre, using established data-reduction [7] and least-squares refinement [8] programs. Weighting points used in setting up the off-diagonal weight matrix used in refinements are given in Table 1, together with scale factors and correlation parameters. In all calculations the scattering factors of Schäfer *et al.*[9] were used. The electron wavelength [5.610(3) pm] was determined by analysis of the diffraction pattern of gaseous benzene.

Structure Refinement.—During refinement of the structure of germyl monothioacetate it was assumed that $SGeH_3$ and CCH_3 groups each had local C_{3v} symmetry, and that the three bonds to the central carbon atom were coplanar. The geometry was then defined by six bond lengths, five valence angles, and three dihedral angles. The GeH_3 and CH_3 twist angles were defined to be zero when one Ge–H or C–H bond was staggered with respect to the C–S bond, while the angle describing the twist about the C–S bond was defined to be zero when the C=O and Ge–S bonds were *cis* with respect to each other.

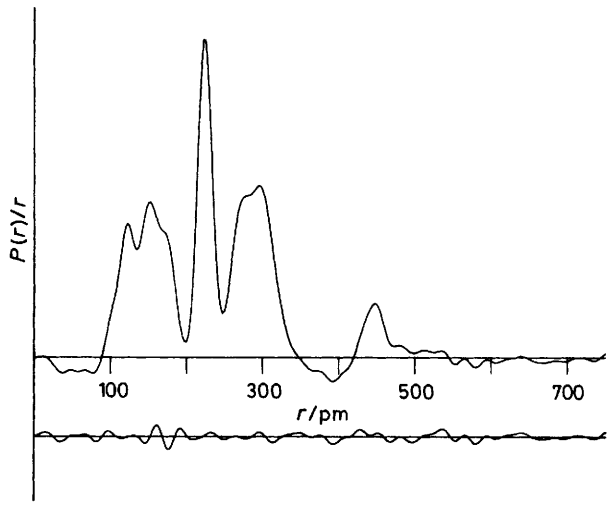

Figure 1. Observed and final difference radial distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.000\,02\,s^2/(Z_{Ge} - f_{Ge})(Z_S - f_S)]$

Although the radial distribution curve (Figure 1) was dominated by the large Ge–S peak, there were three other peaks in the region associated with bonded distances, and it was possible to refine all bonded distances except Ge–H. In a series of refinements with this parameter fixed at various values, the lowest R factor was found when it was set at 152.5. pm, and this value was assumed in subsequent refinements. Similar methods were used to find optimum values of the three angles describing the conformation of the molecule. The three valence angles involving heavy atoms all refined normally, but the SGeH and CCH angles would not refine satisfactorily, and were therefore fixed at 110°.

Results and Discussion

The molecular parameters for germyl monothioacetate are given in Table 2: errors quoted (in parentheses) are estimated

Table 1. Weighting functions, scale factors, and correlation parameters

Camera height / mm	Δs	$s_{min.}$	sw_1 / nm^{-1}	sw_2	$s_{max.}$	Correlation parameter	Scale factor
128.29	4	76	84	220	296	0.328	0.883(30)
286.11	2	44	58	120	146	0.042	0.923(16)

Table 2. Molecular parameters

	Distance (pm)	Amplitude (pm)		Distance (pm)	Amplitude (pm)
(*a*) Independent distances					
r_1 (C–C)	149.3(10)	5.0 [a]	r_4 (C–S)	176.5(7)	4.8 [a]
r_2 (C–H)	108.7(12)	6.5 [a]	r_5 (Ge–S)	223.3(4)	5.7(4)
r_3 (C=O)	122.4(8)	3.9 [a]	r_6 (Ge–H)	152.5 [b]	8.8 [a]
(*b*) Dependent distances					
d_7 (C · · · O)	235.1(18)	8.0 [a]	d_{10} (Ge · · · C)	300.4(8)	10.9(13)
d_8 (S · · · C)	277.3(14)	7.3(14)	d_{11} (Ge · · · C)	445.6(10)	8.5(12)
d_9 (S · · · O)	265.3(12)		d_{12} (Ge · · · O)	297.2(14)	15.0 [a]
(*c*) Angles (°)					
1 (CCO)	116.4(13)		5 (CCH)	110.0 [a]	
2 (SCO)	124.1(10)		6 (twist GeH_3)	5.0 [b]	
3 (GeSC)	96.7(4)		7 (twist CH_3)	40.0 [b]	
4 (SGeH)	110.0 [a]		8 (dihedral GeSCO)	5.0 [b]	

[a] Fixed. [b] See text.

Table 3. Portion of least-squares correlation matrix showing off-diagonal elements greater than 30%

		Angle					
r_2	r_3	1	2	3	u_8	k_1	
34	30	−62	48	−40			r_1
		−43				36	r_4
					−38		r_5
			−58	−73	−67		1
				−70	53	−32	2 } Angle
					−56		3
						55	u_5

standard deviations obtained in the least-squares analysis, increased to allow for systematic errors. Part of the least-squares correlation matrix is given in Table 3. The most significant correlations are between the three refined angles, and arise from the overlap of the associated non-bonded distances, most of which lie between 260 and 300 pm. The intensity data are illustrated in Figure 2, together with the difference curves for the final refinement, for which the R factor (R_G) was 0.11.

The refined data provide clear evidence that germyl monothioacetate exists essentially completely as the S-bonded isomer in the gas phase. No attempt was made to allow for small proportions of the O-bonded isomer in the refinements, as the radial-distribution difference curve (Figure 1) shows no significant features. This observation is supported by spectroscopic evidence.[4]

The geometrical parameters for germyl monothioacetate (Table 2) are much as would be expected, although there are some small differences between our results and those reported for related compounds that may be significant. The C–S distance [176.5(7) pm] is shorter than that in dimethyl sulphide [10] [180.2(2) pm], but the difference is only about half as great as that between C–O distances in esters such as methyl acetate [2] and in dimethyl ether.[11] The Ge–S distance [223.3(4) pm] is greater than in digermyl sulphide [12] [220.9(4) pm], and associated with this there is a narrowing of the angle at sulphur from 98.9(1) to 96.7(4)°. These changes are in the same direction as, but much smaller than, changes in Si–O distances and angles at oxygen in going from disilyl ether [13] to silyl esters.[1-3] The origins of these structural changes are not yet apparent, but a fairly consistent pattern is emerging, and we intend to study esters with germanium bound to oxygen, and with silicon bound to sulphur, to gain greater understanding of the factors that influence structure.

As with all the esters we have studied,[1-3,14] the heavy-atom skeleton is planar: the apparent small deviation from planarity is almost certainly a shrinkage effect. Thus the non-bonded Ge · · · O distance is very much shorter [297.2(14) pm] than the sum of van der Waals radii for germanium and oxygen (*ca.* 360 pm). Ths shortening is not as great as those we have observed for silyl esters (*ca.* 80 pm), but must nevertheless indicate that there is a strong interaction between germanium and oxygen. It is unfortunate that in this case we have been unable to determine the structure of this compound in the crystalline phase, and so study intermolecular Ge · · · O contacts, but it is hoped that the problems will be overcome with other germyl esters.

The Question of O-Bound Germyl Monothioacetate.—We studied the reaction between silyl monothioacetate and

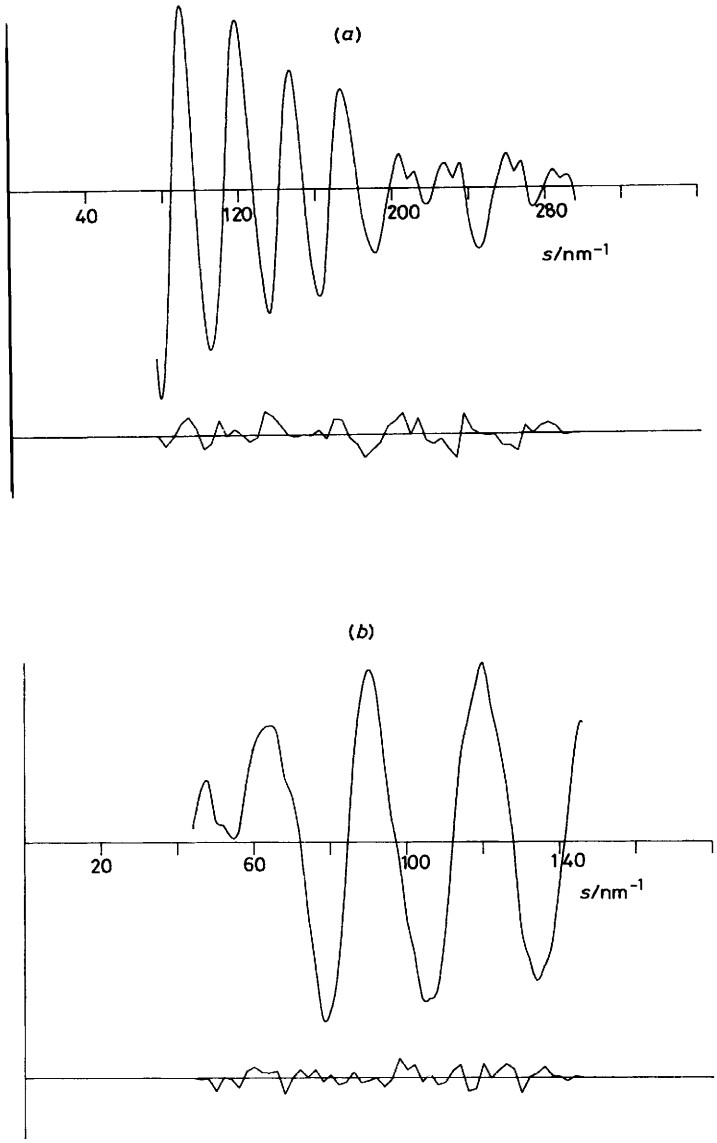

Figure 2. Observed and final weighted difference molecular scattering intensities at nozzle-to-plate distances of (*a*) 128 and (*b*) 286 mm

germyl fluoride by proton n.m.r. spectroscopy at low temperature to see if we could detect any of the O-bound isomer of germyl monothioacetate as an intermediate in the formation of the S-bound compound. From the proton resonance spectra of GeH_3 and SiH_3 compounds, we expected that the proton resonance of the GeH_3 group in the O-isomer would be near that observed for $(GeH_3)_2O$, whose chemical shift is about 5.30 p.p.m.[15] The GeH_3 resonance of the S form is close to that of $(GeH_3)_2S$, at 4.60 p.p.m.[15] The quality of the proton resonance spectra obtained at 180 K was poor, but sufficient to show that even at so low a temperature substantial reaction had occurred. Good quality spectra were obtained from 193 K upwards, and no peaks were observed that could plausibly be assigned to the O-bound isomer. At 193 K reaction appeared to be complete, and so if any of the O-bound isomer is formed it must rearrange to give the S-bound isomer too rapidly for us to detect. The proton chemical shifts for $CH_3COSGeH_3$ in toluene solution at 183 K are δH(C) 1.89 and δH(Ge) 4.32 p.p.m.

We also determined the i.r. spectrum of germyl monothioacetate in the gaseous and solid phases in order to see whether there were any substantial shifts in frequency with change in phase or whether new bands appeared in the spectrum of the solid. Our results are given in Table 4. In general there are shifts to lower frequency from the gas to the solid phase, but these are quite consistent with shifts observed in the spectra of other esters, including methyl acetate. Indeed, the shift in the CO-stretching mode is smaller for germyl thioacetate than for methyl acetate. There was no evidence from the i.r. spectrum for any change in structure from gas to solid or for unusually strong intermolecular interactions in the solid state. Furthermore, there is no splitting in the CO stretch such as would have been expected if the solid contained both *cis* and *trans* isomers.

We also recorded the mass spectrum. The principal fragments with their approximate relative intensities are given in Table 5. The fragmentation pattern is consistent with the structure we have given.

Table 4. Infrared spectra (cm^{-1}) of $CH_3COSGeH_3$

Gas	Solid	Assignment
2 130s	2 128s	$\nu_{asym}(GeH)$
2 108s	2 102s	$\nu_{sym}(GeH)$
1 709s	1 678vs	$\nu(C{=}O)$
	1 415m	$\delta_{asym}(CH)$
1 361m	1 354s	$\delta_{sym}(CH)$
	1 261w	$\delta(CH)$
1 132s	1 128s	$\rho(CH_3)$
1 088vw	1 095m	
1 018w	1 019w	$\rho(CH_3)$
955m	955s	$\nu(C{-}C)$
874m	854s	$\delta(GeH_3)$
862m		
817vs	807vs	$\delta(GeH_3)$
811vs	793vs	$\delta(GeH_3)$
625s	629s	$\nu(C{-}S)$
585w	593m	$\rho(GeH_3)$
466w	471 } m	Deformation CCOS
426w	417 }	
291w	296m	$\nu(Ge{-}S)$

s = Strong, m = medium, w = weak, and v = very.

Spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The solid phase was annealed until there was no further change in the spectrum.

Acknowledgements

We thank the S.E.R.C. for financial support: in particular, we thank Dr. M. Elder and his staff at the S.E.R.C. laboratory, Daresbury, for their helpfulness in providing the microdensitometry service.

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Table 5. Mass spectrum of $CH_3COSGeH_3$ [a]

Ion [b]	m/e	Relative intensity
$[^{74}GeH_3SOCCH_3]^+$	152	20
$[^{74}GeSC]^+$	118	22
$[^{74}GeS]^+$	106	20
$[^{74}Ge]^+$	74	14
$[COS]^+$	60	2
$[CS]^+$	44	13
$[CH_3CO]^+$	43	100
$[CCO]^+$	40	11
$[CO]^+$	28	99
$[CH_3C]^+$	27	7
[GeO]	90	2

[a] Recorded on an MS902 spectrometer, with ionising voltage of 70 eV (*ca.* 1.12×10^{-17} J). Exact mass measurements of parent ion gave 151.935 73 (error 4 p.p.m.). [b] Fragments containing Ge all show a pattern reflecting the relative abundance of the Ge isotopes.

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Received 6th October 1982; *Paper* 2/1725