Journal of Organometallic Chemistry, 281 (1985) 63–68
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE MOLECULAR STRUCTURE OF GERMYL ACETATE IN THE GAS PHASE, DETERMINED BY ELECTRON DIFFRACTION *

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(Received August 1st, 1984)

Summary

The molecular structure of germyl acetate in the gas phase has been determined by electron diffraction. Principal parameters (r_a) are: r(Ge–O) 183.0(4), r(C–O) 135.7(5), r(C=O) 122.9(5), r(C–C) 154.9(9) pm, $<$GeOC 113.0(5), $<$O–C=O 124.0(6), $<$C–C–O 110.3(5)°. The molecule adopts a *cis*-planar conformation with the Ge–O bond eclipsing the C=O bond.

Introduction

The molecular structures of silyl esters and thioesters are characterised by short non-bonded interactions between silicon and neighbouring oxygen or sulphur atoms. In the gas phase, there are short Si $\cdots$ O contacts in silyl formate [1] and silyl acetate [2], and a corresponding Si $\cdots$ S contact in silyl monothioacetate [3] (in which the silyl group is bonded to oxygen). In crystalline phases of the acetate and monothioacetate the short intra-molecular interactions are still present, but there are also inter-molecular Si $\cdots$ O or Si $\cdots$ S contacts. The distances between the atoms involved, for intra- and inter-molecular interactions, are generally some 70–80 pm less than the sum of the appropriate Van der Waals radii.

Germyl esters have been less extensively studied. In germyl monothioacetate [4] the germyl group is bound to sulphur, and in the gas phase the Ge $\cdots$ O distance is 297 pm, much less than the sum of Van der Waals radii (360 pm). However, no gas phase structure has been reported for a simple germyl ester. We have therefore studied germyl acetate by electron diffraction, and report the results here.

Experimental

A sample of germyl acetate was prepared by the reaction of germyl bromide with tributyltin acetate [5], and was purified by fractional condensation in vacuo. Its

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* Presented as part of a plenary lecture at the "International Symposium on New Vistas in Organometallic Chemistry", Jaipur, India, March 5–9, 1984.

0022-328X/85/$03.30

purity was checked by IR spectroscopy. Electron scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh diffraction apparatus [6], operating at 44 kV, and were obtained in digital form using a Joyce-Loebl Microdensitometer 6. The densitometer locates the centre of each pattern automatically and then scans in circles, the radii of which correspond to the desired s values [7].

During experiments the sample and nozzle were maintained at 293 K, and three plates were obtained at each of two camera distances, 285 and 128 mm. Plates were also obtained for benzene gas, and by analysis of these the electron wavelength (5.715 pm) was obtained.

All calculations were carried out on an ICL 2976 computer using established data reduction [7] and least-squares refinement [8] programmes. Weighting points, used in setting up the off-diagonal weight matrix used in the refinements, are given in Table 1, together with other pertinent data. In all calculations, the scattering factors of Schäfer et al. [9] were used.

Structure refinement

During refinements of the structure of germyl acetate it was assumed that the CCH_3 and $OGeH_3$ groups had local C_{3v} symmetry, and that the three bonds to the central carbon atom were coplanar. Three twist angles were used to describe the conformation. The angle for the C–O bond was zero when the C=O and Ge–O bonds eclipsed each other. 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–O bond. The other parameters were six bond lengths and five valence angles, as listed in Table 2.

The radial distribution curve (Fig. 1) shows three peaks corresponding to bonded distances. The first contains contributions from C–H, C=O and C–O bonds. It was possible to refine the three distances, but it was necessary to fix the C–H amplitude of vibration, and to fix the ratio of the other two amplitudes. The second peak arose from C–C and Ge–H bonds, and again both distances could be refined, but the two amplitudes of vibration had to be constrained to maintain a fixed ratio. The third peak was associated with the Ge–O bond, and the distance and amplitude of vibration both refined without problems.

The next part of the radial distribution curve contains a peak associated mainly with non-bonded C $\cdots$ O and C $\cdots$ C atom pairs and one which includes major contributions from Ge $\cdots$ C and Ge $\cdots$ O distances. The maximum of the latter peak is at 270 pm, and it is clear that the Ge $\cdots$ O distance is substantially less than 300 pm, although the sum of Van der Waals [6] radii is 360 pm. The only other major peak is that representing the long Ge $\cdots$ C distance, near 410 pm. There was sufficient information available in the positions, widths and shapes of these peaks to

TABLE 1

SCALE FACTORS, CORRELATION PARAMETERS AND WEIGHTING FUNCTIONS

Camera height (mm)	Δs	s_{min}	sw_1	sw_2	s_{max}	Correlation parameter	Scale factor
	(nm^{-1})						
285.2	2	20	40	90	100	0.216	0.731(12)
128.5	4	68	90	280	328	−0.331	0.979(56)

enable the heavy-atom valence angles to be determined. Amplitudes of vibration were also refined for the Ge ··· O and the two Ge ··· C distances, and a single value was obtained for the group of C ··· O and O ··· O distances. This last value (4.6(11) pm) was somewhat smaller than expected, but when refinements were performed with it set at higher values, up to 9 pm, there was very little change in other parameters. The three torsion angles were investigated by doing series of

TABLE 2

MOLECULAR PARAMETERS (p) [a]

Distances r (pm)		
p1	r(C–C)	154.9(9)
p2	r(C–H)	109.6(11)
p3	r(C=O)	122.9(5)
p4	r(C–O)	135.7(5)
p5	r(Ge–O)	183.0(4)
p6	r(Ge–H)	155.6(15)
Angles (°)		
p7	< (C–C–O)	110.3(5)
p8	< (O=C–O)	124.0(6)
p9	< (C–O–Ge)	113.0(5)
p10	< (O–Ge–H)	110.0(fixed)
p11	< (C–C–H)	107.4(48)
Twist angles (°)		
p12	C–O	0.0(fixed) [b]
p13	O–Ge	0.0(fixed) [b]
p14	C–C	20.0(fixed) [b]

[a] Uncertainties, quoted in parentheses, are estimated standard deviations increased to allow for systematic errors. [b] Series of refinements were performed with these parameters set at various values. They were subsequently fixed at the optimum values.

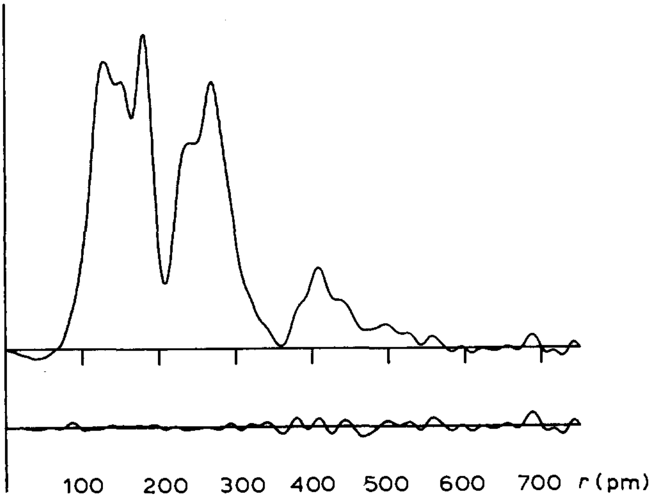

Fig. 1. Observed and final difference radial distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s \times \exp[-0.00002s^2/(Z_{Ge}-f_{Ge})(Z_O-f_O)]$.

refinements with them fixed at various values, and comparing R factors. In subsequent refinements they were fixed at the optimum values.

In the final refinement, for which R_G was 0.11, the parameters listed in Table 2 were obtained. The interatomic distances (r_a) and vibrational amplitudes are given in Table 3, and major elements of the least-squares correlation matrix are listed in

TABLE 3

INTERATOMIC DISTANCES (r) AND AMPLITUDES OF VIBRATION (pm)

Atoms	Distance	Amplitude
C–C	154.9(9)	4.9(5)
C–H	109.6(11)	7.0(fixed)
C=O	122.9(5)	4.6(11)
C–O	135.7(5)	5.4(tied to u3)
Ge–O	183.0(4)	6.4(6)
Ge–H	155.6(15)	9.7(tied to u1)
C · · · O	247.7(9)	4.6(11)
C · · · O	238.7(8)	
O · · · O	228.4(6)	
Ge · · · C	267.1(8)	7.2(7)
Ge · · · C	408.1(10)	16.5(18)
Ge · · · O	283.9(12)	14.8(14)
Ge · · · H	480.1(49)	40.0(fixed)
Ge · · · H	426.6(64)	
Ge · · · H	445.9(58)	

Note: Other C · · · H, O · · · H and H · · · H non-bonded distances were included in the refinements, but are not listed here

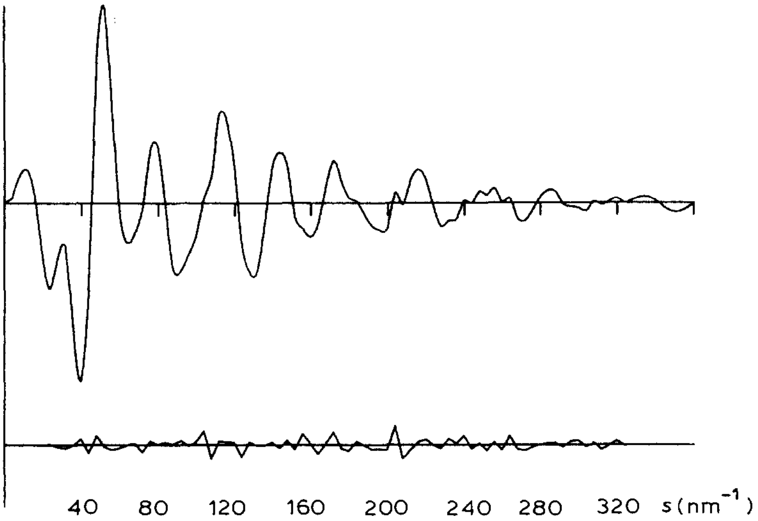

Fig. 2. Observed and final weighted difference combined molecular scattering intensity curves.

Table 4. The intensity data, and final difference curve, are shown in Fig. 2, while Fig. 3 shows a perspective view of a molecule.

Discussion

The general features of the structure of germyl acetate are in accord with those of other silyl and germyl esters. The germyl group eclipses the C=O bond, the non-bonded distance between the germanium and oxygen atoms is short, the Ge–O bond is long, and the angle GeOC is narrow. But all these features are more exaggerated in the present case. Thus the Ge–O bond length is 183.0(4) pm compared with 176.6(4) pm in $O(GeH_3)_2$ [10], and this is actually greater than a value obtained from covalent radii derived from bond lengths in ethane, dimethyl ether, and digermane. There are few Ge–O distances in the literature for comparison, but other long ones have been reported for another ester, triphenylgermyl trifluoroacetate [11] (186.6 pm), for triphenylgermyl(triphenyltin)ether [12] (183.9 pm) and a platinum complex having a hydroxydiphenylgermyl ligand [13] (184.6 pm): typical distances are 173–177 pm. The GeOC angle in germyl acetate is

TABLE 4

LEAST-SQUARES CORRELATION MATRIX ×100 [a]

p3	p6	p8	p10	u3	$k2$ [b]	
	−83	67				p1
60					−53	p2
	63		69			p5
		−62			−50	p6
				60		u1
					86	u5
		−60				u12

[a] Only elements with absolute values ≥ 50 are given. [b] Scale factor for data set 2.

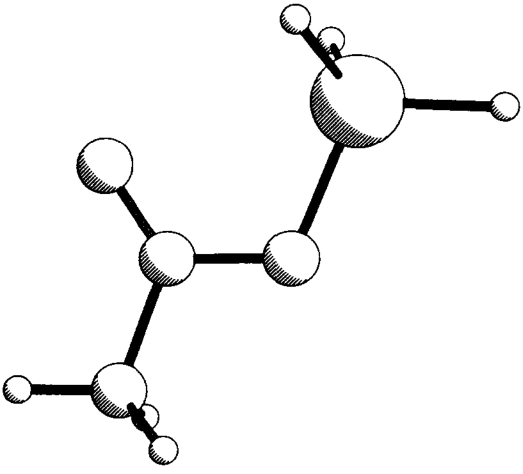

Fig. 3. Perspective view of a molecule of germyl acetate.

113.0(5)°, which is very narrow for an oxygen atom bound to a silyl or germyl group. The corresponding angle in digermyl ether [10] is 126.5(3)°, but in silyl esters the SiOC angles are also quite small, 116–118° [1–3].

The most remarkable feature of this structure is the short non-bonded Ge · · · O interaction 283.9(12) pm. The equivalent distance in silyl acetate is 279.5(14) pm [2], but as the Van der Waals radius for germanium is ca. 10 pm greater than that for silicon, the interaction in the germyl ester must be stronger than that in the silyl ester. In the solid phase, silyl acetate also has intermolecular contacts between silicon and oxygen atoms, and it is unfortunate that we have been unable to obtain crystallographic data for germyl acetate.

In other respects the parameters in Table 2 are much as would be expected. The C–C distance is somewhat longer than in other acetates, and the C–C–O angle is rather small, but as there is a strong Ge–H contribution at almost the same place as the C–C peak in the radial distribution curve, there must be some uncertainty about these particular parameters.

Acknowledgement

We thank the S.E.R.C. for financial support.

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