Diformatosilane: Preparation, Characterisation, and Molecular Structure in the Gas Phase by Electron Diffraction†

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The first bis-ester derivative of silane, $SiH_2(OCHO)_2$, has been prepared and characterised by a variety of spectroscopic techniques and by electron diffraction in the gas phase. The electron-diffraction investigation shows it to have an asymmetric conformation, one formate group apparently being close to the *cis* arrangement about its SiO bond, the other close to *trans*. The two formate groups are, however, equivalent on the n.m.r. time-scale.

Some dialkoxysilanes were prepared and characterised many years ago,[1,2] and 'prosiloxane', $(SiH_2O)_n$, has been shown[3] to consist of a mixture of cyclic species with alternating SiH_2 and oxygen moieties. Nevertheless, there are few reports in the literature of compounds containing two oxygen ligands on an SiH_2 group, and this is probably linked with the chemical lability of SiH bonds and the much greater thermodynamic stability of SiO linkages. Thus SiH_4 and methoxysilanes react[2] with liquid CH_3OH or with gaseous CH_3OH in the presence of copper metal liberating H_2, though mono-, di-, and tri-alkoxysilanes seem to be stable when pure. We have shown[4] that simple silyl esters of organic acids $RCOOSiH_3$, where R = H,CH_3, *etc.*, may be prepared under very mild conditions by mixing silyl halides with trialkyltin esters at or below room temperature, and now report that a similar reaction of a dihalogenosilane with tributyltin formate gives a new compound identified as diformatosilane, $SiH_2(OCHO)_2$. We have characterised it by spectroscopic means and have studied its structure in the gas phase by electron diffraction.

Experimental

Preparation.—Dibromosilane [prepared from dichlorosilane *via* bis(dimethylamino)silane[5]] (5 mmol) was condensed under vacuum into a glass tap ampoule containing tributyltin formate[6] (12 mmol) at 77 K. The ampoule and its contents were allowed to warm to room temperature with vigorous shaking. After about 1 min, when the viscosity of the contents had noticeably diminished, volatile products were removed by condensation at 77 K in a vacuum system. Trap-to-trap distillation gave *diformatosilane* (3.6 mmol, 72%) which was retained at 227 K but passed a trap at 250 K. The same product could be obtained, in slightly lower yield (61%), by reaction of dichlorosilane with tributyltin formate under similar conditions. Diformatosilane is a colourless liquid, vapour pressure 1.4 mmHg at 271.7 K. It was characterised by mass spectrometry, multinuclear n.m.r., i.r., and Raman spectroscopy, and electron diffraction in the gas phase (see below).

Volatile compounds were prepared and handled using a conventional glass vacuum line, and their identity and purity established by study of the i.r. spectra in the gas phase and of ^1H n.m.r. spectra in solution.

Instrumental.—I.r. spectra of gaseous samples were obtained with a Perkin-Elmer 598 recording spectrophotometer, and of solid and matrix-isolated samples with a Perkin-Elmer 225 spectrometer, samples being held at a controlled temperature between 15 and 100 K on a CsI window cooled by an Air Products DE-202 helium microrefrigerator. Raman spectra of liquid samples were obtained using a Cary 83 spectrometer with an argon-ion laser operating at 488 nm as light source. Proton n.m.r. spectra were obtained using a Bruker WP80 spectrometer operating at 80 MHz, and ^{13}C and ^{29}Si spectra using a Bruker WP200 spectrometer operating at 50.32 and 39.76 MHz

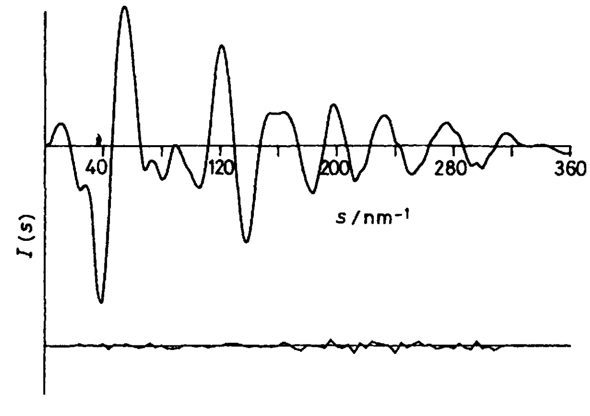

Figure 1. Combined electron-scattering intensities: observed and final difference curves

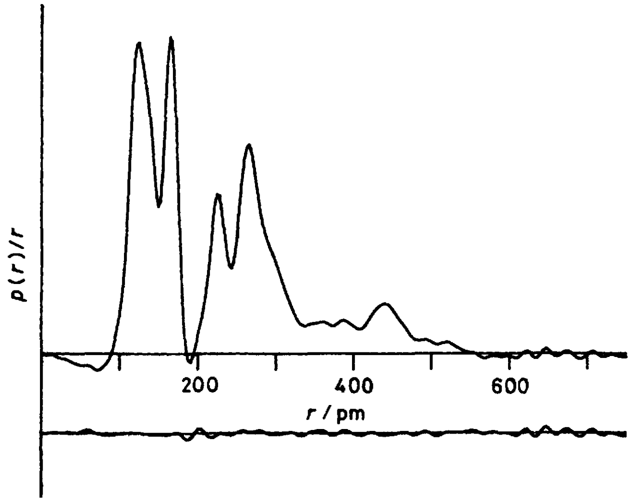

Figure 2. Observed and final difference radial distribution curves. Before Fourier inversion the data were multiplied by $s\cdot\exp[-0.000\,02s^2/(Z_{Si} - f_{Si})(Z_O - f_O)]$

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† *Non. S.I. units employed:* mmHg ≈ 134 Pa, eV ≈ 1.60 × 10^{-19} J.

Table 1. Camera distances/mm, s ranges/nm^{-1}, correlation parameters, and scale factors; electron wavelength = 5.693(6) pm

Distance	s	$s_{min.}$	s_{w1}	s_{w2}	$s_{max.}$	Correlation parameter	Scale factor
285.48	2	20	40	124	144	−0.128	0.639(4)
128.36	4	68	80	300	328	−0.075	0.771(13)

Table 2. Infrared and Raman spectra of $SiH_2(OCHO)_2$; n.o. = not observed

I.r.				
Gas	N_2 matrix	Solid	Raman liquid	Assignment
2 944m	2 969w	2 962w	2 985m	ν(CH); ν_1 and ν_2
2 256ms	2 256mw	2 260ms	2 266s,p	ν(SiH); ν_3, ν_{19}
	2 251(sh)			
1 744vs	1 737vs	1 710vs	1 740m,br	ν(C=O); ν_4, ν_5
	1 722s		1 720ms	
1 370vw	1 372vw	1 378mw	1 387m	δ_i(CH); ν_6, ν_7
1 188s	1 193ms			
	1 177s		1 200w,br	ν(C–O); ν_8, ν_9
1 162vs	1 165s	1 164vs		
	1 159vs			
n.o.	n.o.	1 040vvw	1 045w	δ_o(CH); ν_{20}, ν_{21}
953ms	954ms	943s	957m	$\delta_s(SiH_2)$; ν_{10}
909(*PR*),vs	898vs	889vs	908w	$\delta_w(SiH_2)$; ν_{11}
	805m	800	800m	
768m	777m	774ms	760m	ν(SiO); ν_{12}, ν_{13}
	771	754	710vs,p	
	730			
715(*PQR*)w	714w	696ms	n.o.	$\delta_t(SiH_2)$; ν_{22}
	693			
640w	642w	644m	640w	δ(OCO); ν_{14}, ν_{15}
550w	477vw?	537w	551mw	$\rho(SiH_2)$; ν_{23}
	355w	354m		
320vvw	314w	318m	325vw	δ(OSiO); ν_{16}
	249w	268m		
	228w			τ(CO); ν_{24}, ν_{25}
			170vw	δ(SiOC); ν_{17}, ν_{18}

respectively. The mass spectrum was obtained using an AEI MS902 spectrometer, using 70-eV electron energy.

Electron-diffraction experiments used the Edinburgh apparatus,[7] data being recorded photographically and converted into digital form by the S.E.R.C.-funded microdensitometer service at Daresbury.[8] The data reduction[8] and model refinement[7] were performed with established programs. The sample and nozzles were at 293 K during experiments; three plates were exposed at each of two camera distances, 128 and 285 mm, giving data over a range of 20—328 nm^{-1} in the scattering variable s. The s ranges, weighting points, correlation parameters, scale factors, and electron wavelengths (calculated from diffraction patterns of benzene recorded consecutively with those of the compound) are given in Table 1. The scattering factors of Schäfer *et al.*[9] were used in all calculations. A curve showing the combined intensities and a radial distribution curve are shown in Figures 1 and 2, with the final differences between observed and calculated intensities or $P(r)/r$ shown in each case.

Characterisation.—N.m.r. spectra. Proton, ^{13}C, and ^{29}Si n.m.r. spectra were recorded, giving the following parameters: $\delta(CH)$ 7.12, $\delta(SiH)$ 4.58, $\delta(^{13}C)$ 158.2, and $\delta(^{29}Si)$ −35.5 p.p.m. (all relative to $SiMe_4$); $^1J(CH)$ 233.1, $^1J(SiH)$ 281.6, $^3J(SiH)$ 6.8, and $^4J(HH)$ 0.5 Hz. No ^{13}C satellites of the Si*H* resonance were observed, so $^3J(CH)$ is not determined. The two CH protons are effectively equivalent at room temperature. A triplet of triplets in the ^{29}Si spectrum confirms the formulation of the compound as $SiH_2(R_H)_2$, where R_H contains a single proton and is identified as the formate group from its proton and ^{13}C chemical shifts.

Mass spectrum. There was a weak molecular ion peak at m/e = 120, with a strong fragment-ion peak at m/e = 91, corresponding to loss of HCO from the molecular ion. A weaker fragment-ion peak at m/e = 75 is attributable to loss of HCO_2 from the molecular ion, showing that both C–O and Si–O bond cleavage occurs. The $(M + 1)^+$ peak at m/e = 121 was nearly as strong as the molecular ion peak.

Reactions. Some exchange reactions of diformatosilane were investigated using ^1H n.m.r. spectroscopy, small quantities of reactants being mixed in n.m.r. tubes with [$^2H_8$]toluene as solvent and standard. Reactions with SiH_3X (X = Cl or Br) gave $SiH_3(OCHO)$, SiH_2X_2, and a new species in each case, identified on the basis of its ^1H n.m.r. spectrum as $SiH_2X(OCHO)$ [X = Cl, $\delta(SiH)$ = 4.69 and $\delta(CH)$ = 7.05 p.p.m., $^1J(SiH)$ = 286.3, $^1J(CH)$ = 235.6, and $^4J(HH)$ = 0.5 Hz; X = Br, $\delta(SiH)$ = 4.75 and $\delta(CH)$ = 7.02 p.p.m., $^1J(SiH)$ = 287.4 and $^4J(HH)$ = 0.5 Hz]. The same product was also observed in each case when $SiH_2(OCHO)_2$ was mixed with SiH_2X_2. No exchange products were observed when $SiH_2(OCHO)_2$ was mixed with GeH_3X (X = Cl or Br) under the same conditions, but a complex mixture of products was found when it reacted with GeH_3F. The compound $SiH_2F(OCHO)$ was tentatively identified by its ^1H and ^{19}F n.m.r. spectra [$\delta(SiH)$ = 4.31 and $\delta(F)$ = −160.3 p.p.m.; $^1J(SiH)$ = 283.7, $^2J(HF)$ = 58.0, $^4J(HH)$ = 0.6, and $^4J(HF)$ = 1.8 Hz]. The C*H* signal could not be identified with any certainty among a group of signals due to various formate-containing species.

Results and Discussion

Vibrational Spectra.—The i.r. and Raman bands recorded for samples of $SiH_2(OCHO)_2$ under various conditions are listed in Table 2, together with a suggested assignment. This assumes a structure based on that found by electron diffraction (see below), idealised so that the two (non-identical) formate groups have a common plane of symmetry. The molecular symmetry is then C_s, and the 27 normal modes are expected to be separable into 18 of a' symmetry and 9 of a'' symmetry. The latter will give rise to a dipole change perpendicular to the plane of symmetry and hence should give type C band contours in the i.r. spectrum of the gas. The only band to show any distinguishable Q branch is the weak band at 715 cm^{-1}, which is therefore assigned to an a'' mode, probably the SiH_2 torsion, which is i.r. active in this molecule solely because of the non-equivalence of the two formate groups. This non-equivalence is also manifested in the clear doubling of the characteristic ν(C–O) bands just below 1 200 cm^{-1} in the gas phase and in the matrix. In the gas phase the other formate modes [ν(CH), ν(C=O), and δ(OCO)] and ν(SiO) give only a single band in each case, but splittings are apparent in some cases in the matrix. The band associated with ν(SiO) splits into several components in the solid and liquid phases as well; the Raman band of the liquid at 710 cm^{-1} is the strongest in the spectrum and is distinctly polarised, so must be assigned to this mode rather than the SiH_2 torsion, whose Raman band is presumably hidden by the stronger ν(SiO) band. This suggests that there may be a change in the conformation, or a mixture of conformations may occur, in the condensed phases, but there is no evidence as to the nature of the conformation(s) in the liquid and solid. The OSiO deformation is assigned to very weak i.r. and Raman bands near 320 cm^{-1}, very close to δ(SiF_2) for SiH_2F_2 at 322 cm^{-1}.[10]

Other assignments are mainly by analogy with those for silyl formate[4,11] or other SiH_2 compounds.[12] The assignment is almost complete down to 500 cm^{-1}; all fundamentals expected can be assigned in each spectrum, except that the out-of-plane CH deformations of the formate groups are not discernible in the i.r. spectra of the gaseous and matrix samples. A distinct but very weak band in the i.r. spectrum of the solid and a weak band in the Raman spectrum of the liquid are assigned to the expected modes for the two formate groups. Below 500 cm^{-1} we expect three in-plane modes (two SiOC bends and the OSiO bend) and four torsions of a'' symmetry, derived from twisting motions about the C–O and Si–O bonds. As mentioned above, δ(OSiO) can plausibly be assigned near 320 cm^{-1}; the SiOC bonds may be expected below 200 cm^{-1}, and are not observed in our i.r. spectra as a result. An indistinct Raman band on a rapidly rising background near 170 cm^{-1} may be due to one or both of these motions. The CO torsion in silyl formate has been assigned[4] to a weak band at 223 cm^{-1}, and weak bands in the matrix at 249 and 228 cm^{-1} may be due to the corresponding modes here. A moderate band in the i.r. spectrum of the solid at 268 cm^{-1} is probably related, as torsions are often increased in frequency in condensed phases. The SiO torsions give no detectable bands in the i.r. spectrum above 200 cm^{-1} or in the Raman spectrum and remain unassigned. Table 3 shows the very close agreement between the assignments for $SiH_2(OCHO)_2$ and $SiH_3(OCHO)$.[4,11]

Table 3. Corresponding modes of mono- and di-formatosilanes

$SiH_2(OCHO)_2$	$SiH_3(OCHO)$	
2 944	2 945	ν(CH)
1 744	1 750	ν(C=O)
1 370	1 376	δ(CH) in plane
1 188 1 162	1 195	ν(C–O)
768	808	ν(SiO)
640	720?	δ(OCO)
249 228	223	τ(CO)
170	160	δ(SiOC)

Molecular Structure in the Gas Phase.—The results of electron diffraction from a gaseous sample were used to define the molecular structure. The model used assumed planar OCHO groups with identical bond lengths and angles, but allowed independent variation of the torsion angles about the two SiO and the two CO bonds. It proved impossible to fit the data adequately unless the two SiO torsion angles differed by about 180°, so that one C–O–Si–O linkage was close to *cis*, the other close to *trans*, though both Si–O–C=O groups were close to the *cis* conformation (see Figure 3). The resulting Si ⋯ O=C non-bonded contacts were therefore similar to that found[13] for silyl formate. The two formate groups are not related by symmetry and the molecular structure has no two-fold rotation axis, and apparently not even a mirror plane. This latter feature may simply be due to the shrinkage effects associated with the very low-frequency torsional motions, and we have shown above that the assumption of an idealised molecular structure of C_s symmetry with non-identical formate groups allows us to interpret the vibrational spectra.

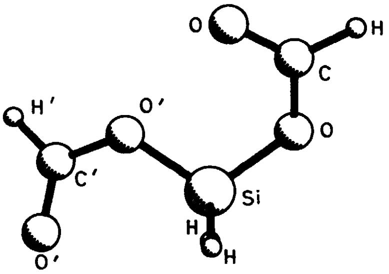

Figure 3. Idealised conformation of $SiH_2(OCHO)_2$

The refined molecular parameters (Table 4) are reasonable, though some of the non-bonded interatomic distances are shorter than those calculated on the basis of normal van der Waals radii. The very short Si ⋯ O=C and two-bond O ⋯ O distances (*ca.* 290 and 225 pm respectively) are expected,[13] but there is also a close approach between the carbonyl oxygen of the *cis* formate group and the other single-bonded oxygen of 261 pm, which is much less than the sum of van der Waals radii, 280 pm. It is therefore necessary to suppose that the *cis* conformation is favoured by other factors, despite this close contact. The effective equivalence of the two formate groups on the n.m.r. time-scale shows that the conformations must interchange. The present static but asymmetric model fits the data well, with final R factors of 5.3 (R_G) and 5.9% (R_D).

The final amplitudes [Table 4(*c*)] for non-bonded distances involving non-hydrogen atoms have all been refined at some stage in the analysis, but we cannot claim them to be a unique set all of which are simultaneously determined. It is clear that some very large amplitudes are necessary, and attempts to constrain, for instance, the two non-bonded SiO amplitudes to a common value worsened the fit considerably, though the overall solution still seemed acceptable. The values reported here are those giving the best fit to the data that we have found; if anything the

Table 4. Model parameters (r_a) for diformatosilane

(*a*) Bond lengths/pm		$SiH_3(OCHO)$
SiH	151.6(11)	150.0(8)
SiO	166.7(3)	169.5(3)
C–O	136.9(3)	135.1(6)
C=O	121.4(2)	120.9(7)
CH	110.6 (fixed)	112(4)
(*b*) Bond angles/°		
HSiH	110 (fixed)	
OSiO	109.3(25)	
SiOC	120.4(4)	116.8(5)
OCO	121.3(3)	123.5(5)
HCO	120 (fixed)	110 (fixed)
SiO torsion	212(7)	
SiO′ torsion	−27(7)	
OC torsion	169(10)	201(3)
O′C′ torsion	207(9)	

(*c*) Interatomic distances and amplitudes/pm

	r_a	u			r_a	u	
SiH	151.6	7.7	f*	H″···H″	248.4	10	f
SiO	166.7	5.1(1)		H″···O	260.0	11	f
C–O	136.9	5.4(2)		H″···C	338.7	15	f
C=O	121.4	4.1(2)		H″···C	382.5	15	f
CH	110.6	7.0	f	H″···C	339.2	15	f
O···O	225.3	6.3(2)		H″···C	296.7	15	f
Si···C	263.9	8.2(3)		H″···O	355.9	20	f
O···O	272.0	42	f*	H″···O	422.3	20	f
Si···O	288.2	15.0(9)		H″···O	334.3	20	f
Si···O	292.8	46.3	f*	H″···O	286.8	20	f
O···C	303.6	15.6	f*	H″···H	428.4	20	f
O···C	395.5	45.6	f*	H″···H	471.4	20	f
O···O	260.7	20.8	f*	H″···H′	445.4	20	f
O···O	449.9	18.7	f*	H″···H′	389.3	20	f
C···C	438.5	12.2	f*	H···O	201.0	10	f
O···O	484.5	27.8	f*	H′···O	213.3	10	f
C···O	390.8	16.0	f*	H···Si	364.4	15	f
C···O	517.3	16.8	f*	H′···Si	360.9	15	f
				H′···O′	413.6	20	f
				H′···O	471.6	20	f
				H···C′	547.8	20	f
				H′···C	495.3	20	f
				H···O′	626.9	25	f
				H′···O	432.2	25	f
				H···H′	600.1	25	f

f = Fixed at this value throughout refinement; f* = fixed after refining to this value.

Table 5. Least-squares correlation matrix (× 100); t = torsion

	Angle OCO	t(SiO)	*u*(C–O)	*u*(Si···O)	Scale 2
r(SiH)			−65		
r(C–O)	−61				
Angle OSiO		−84			
Angle SiOC		−57			
t(CO)		−67			
u(Si–O)					60
u(C=O)			68		
u(Si···C)				57	

Only off-diagonal elements whose magnitude exceeds 50 are shown.

fit is better than expected. The correlation matrix for refining parameters is given in Table 5 in condensed form.

General Discussion and Conclusions.—Diformatosilane, once prepared by an exchange reaction under mild conditions, proves to be reasonably stable, though it is subject to hydrolysis, aerial oxidation, and to other decomposition reactions to give formic acid and other as yet unidentified products. It can be handled *in vacuo*, having a vapour pressure of a few mmHg at room temperature. It undergoes exchange reactions with electronegative groups X on silicon or germanium hydride moieties, yielding mixed compounds $SiH_2X(OCHO)$ (X = F, Cl, or Br) that have as yet been identified only tentatively from ^1H n.m.r. spectra.

The vibrational spectra show clearly the presence of non-identical formate conformations, though on the n.m.r. time-scale the two groups are effectively equivalent. These observations, together with the electron-diffraction evidence for two formate groups with different conformations about their SiO bonds, can be reconciled if a facile interchange of conformation, probably concerted, between the two groups is postulated. (This is equivalent to the existence of a coupled torsional vibration of very low frequency and very high amplitude.) The structure found by analysis of the electron-diffraction data has CO torsion angles slightly different from 180° (defined as *cis*) probably because of shrinkage effects associated with torsional motions. In the same way, the SiO torsion angles depart from 180° (*cis*) and 0° (*trans*), probably for the same reason. The amplitudes of vibration calculated for the non-bonded distances include some very large values (over 40 pm), which is consonant with high-amplitude torsional motions.

Acknowledgements

It is a pleasure to acknowledge the gift of a cylinder of SiH_2Cl_2, used as the starting material in this investigation, by Union Carbide and the help and encouragement given us in the electron diffraction investigations by Drs. D. W. H. Rankin and H. E. Robertson of this Department.

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Received 31*st May* 1985; *Paper* 5/926