Electron-diffraction Investigation of the Molecular Structure of Methyl Chlorosulphate

By **István Hargittai, György Schultz,** and **Mária Kolonits,** Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1088 Budapest, Puskin utca 11-13, Hungary

An electron-diffraction structure analysis has yielded the following bond lengths (r_a) and bond angles of the title compound: S=O 1.419(3), S–O 1.562(4), and S–Cl 2.023(4) Å; Cl–S–O 102.8(14), O–S=O 108.7(8), Cl–S=O 106.4(6), O=S=O 122.2(15), and S–O–C 114.4(11)°. A *gauche* form characterized by a rotation angle of 74° around the S–O bond (0° corresponds to a form in which the O–C bond eclipses the S–Cl bond) prevails in the vapour phase. The sulphur bond configuration is consistent with other simple sulphone structures. Both valence-shell electron-pair repulsions and non-bonded interactions are thought to be responsible for the observed geometrical variations.

AN electron-diffraction investigation of methyl chlorosulphate was initiated as a continuation of our structural studies on simple sulphone molecules that include SO_2Cl_2,[1] $MeSO_2Cl$,[2] $MeSO_2F$,[3] Me_2SO_2,[4] $PhSO_2Cl$,[5] and Me_2NSO_2Cl.[6] The variations in the sulphur bond configurations show interesting trends most of which can be readily interpreted [3,7] using the valence-shell electron-pair-repulsion (VSEPR) model.[8] The importance of non-bonded interactions is also increasingly recognized in discussing these structures.[4,7]

In addition to the determination of the sulphur bond configuration, the conformational properties of the methyl chlorosulphate molecules seemed to be of interest. Earlier, an electron-diffraction and microwave-spectroscopic investigation of methyl fluorosulphate had been carried out.[9] The presence of a conformer with a symmetry plane was determined unambiguously from the microwave spectrum. This plane contains the F–S–O–C chain. This form was then shown to be the *anti* conformer in the electron-diffraction analysis. The latter indicated that a considerable, though not well determined, amount of a *gauche* form was also present. It seemed to be difficult to establish both the relative abundance of the conformers and the rotation angle characterizing the *gauche* form. These difficulties arise in the electron-diffraction analysis of $SFO_2(OMe)$ mainly because the rotation-dependent F $\cdots$ C and O $\cdots$ C non-bonded interactions contribute nearly equally to the electron scattering.

The molecule $SClO_2(OMe)$ is better suited to an electron-diffraction determination of the conformational properties since the contributions of the most important rotation-dependent distances Cl $\cdots$ C and O $\cdots$ C differ considerably. On the other hand, attempts at a microwave-spectroscopic investigation of $SClO_2(OMe)$ have so far been unsuccessful.†

EXPERIMENTAL

The sample of $SClO_2(OMe)$ was synthesized and kindly provided by Dr. B. Nagel (Leipzig) [10a] and its purity was confirmed by mass spectrometry by Dr. J. Tamás (Budapest).[10b]

The electron-diffraction patterns were taken with an EG-100A apparatus [11,12] with essentially the same techniques that have been used in studying some of the other compounds mentioned in the introduction.[2-4] The nozzle of the so-called membrane-nozzle system was at room temperature during the exposures. The wavelength of the electron beam was determined from the diffraction patterns of thallium(I) chloride.[13]

The ranges of intensity data used were $2.125 \leqslant s \leqslant 12.50$ and $6.25 \leqslant s \leqslant 34.0$ Å^{-1} for the 50- and 19-cm camera ranges with $\Delta s = 0.125$ and 0.25 Å^{-1}, respectively. The experimental intensity data are available as Supplementary Publication No. SUP 22048 (2 pp.).‡ The reduced experimental molecular intensities were obtained as before [2-4] and are shown in Figure 1.

STRUCTURE ANALYSIS

The Geometry of the Models.—The molecule as a whole did not have any symmetry except when the Cl–S–O–C chain was planar. In the latter case the molecule had a symmetry plane (C_s) with $\phi = 0$ and 180° for the *syn* and *anti* forms respectively. The general form with $0 < \phi < 180°$ (*gauche*) is shown by its Newman projection in Figure 2. The CH_3 group had a local C_{3v} symmetry and the three-fold axis coincided with the direction of the C–O bond. The methyl conformation around the C–O bond was such that one of the C–H bonds took the *anti* position relative to the

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† Microwave-spectroscopic data could provide, among other things, the planar moment for the *anti* form if present. This moment would, in turn, yield an accurate value for the O $\cdots$ O (O=S=O) distance. Such information could then greatly facilitate the determination of the sulphur bond configuration, see, for example, refs. 3 and 4.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

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[10] (*a*) B. Nagel, personal communication; (*b*) J. Tamás, *ibid.*

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S–O bond. The independent geometrical parameters are listed in Table I.

Experimental Radial Distribution.—The experimental radial distribution is represented in Figure 3. The bonds C–O, S=O, and S–O contribute to the maximum at r *ca.* 1.42 Å. An expressed asymmetry can be observed originating from the S–O bond. The maximum at 2.02 Å can be readily assigned to the S–Cl bond. A double maximum (2.48 and 2.78 Å) follows under which all the non-bonded distances determining the bond angles, and also some of the rotation-dependent distances, are expected to appear. The relatively small features in the $r > 3.1$ Å region arise from contributions of rotation-dependent distances. When the experimental curve is compared with curves calculated for the *gauche* and the *anti* form (Figure 3) it is seen that the main features of this region can be better approximated with the *gauche* than with the *anti* model.

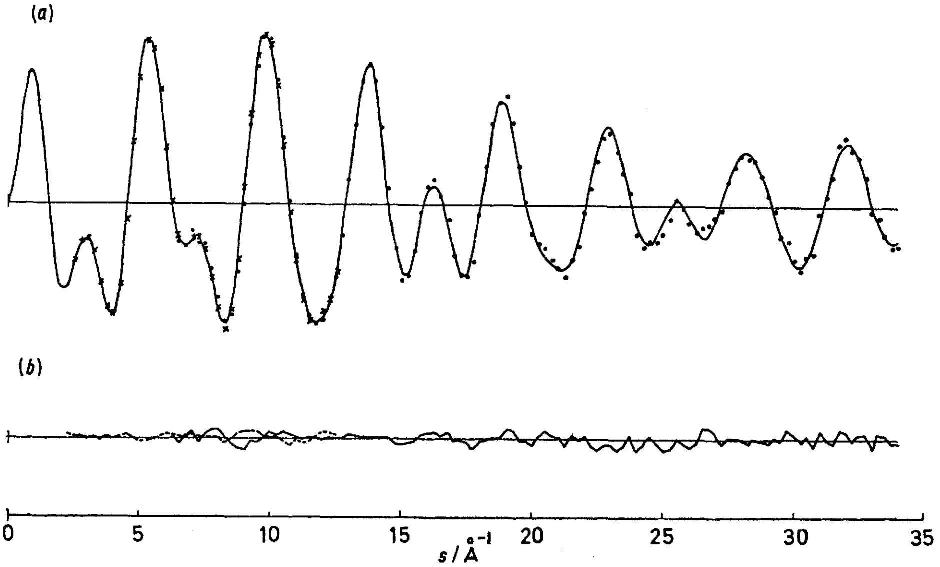

FIGURE 1 (*a*) Experimental (× and ● for 50- and 19-cm camera ranges, respectively) and theoretical (——) molecular intensities for $SClO_2(OMe)$. (*b*) $sM^E(s) - sM^T(s)$. The theoretical curve was computed from the parameters in Table 1

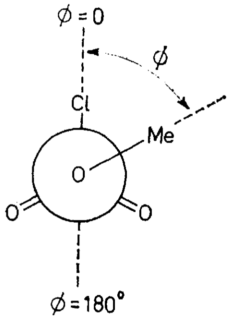

FIGURE 2 Newman projection of the molecular model of $SClO_2(OMe)$ representing a view along the S–O bond. The rotation angle ϕ is also defined

$$sM(s) = \sum_{i}\sum_{j \atop i \neq j} \frac{|f_i(s)||f_j(s)|}{B(s)} \cos[\eta_i(s) - \eta_j(s)] \exp(-\tfrac{1}{2}l_{ij}^2 s^2)\sin[s(r_{ij} - k_{ij}s^2)] \quad (1)$$

Refinements.—The least-squares method was applied to the molecular intensities [14] in the form (1) where $|f(s)|$ and $\eta(s)$ are the absolute values and phases of the complex electron-scattering amplitudes, r_{ij} are the internuclear distances (r_a parameters), and l_{ij} and k_{ij} the corresponding mean amplitudes of vibration and asymmetry constants, respectively; $B(s)$ is the theoretical background. The

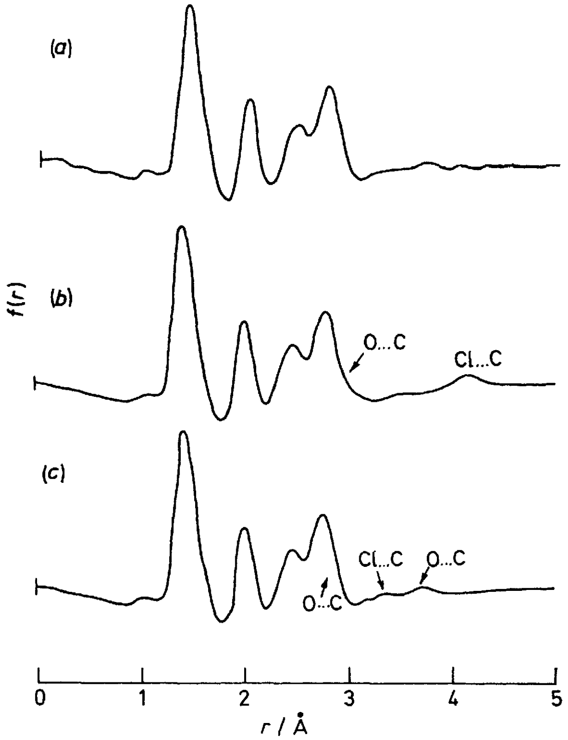

FIGURE 3 Experimental (*a*) and theoretical (*b*) and (*c*) radial distributions for $SClO_2(OMe)$. The artificial damping constant $a = 0.002$ Å^2. Curves (*b*) and (*c*) were computed from the parameters given in Table 1 for the *anti* and *gauche* forms respectively. The positions of the most important rotation-dependent distances are shown

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[14] B. Andersen, H. M. Seip, T. G. Strand, and R. Stølevik, *Acta Chem. Scand.*, 1969, **23**, 3224.

coherent and incoherent scattering amplitudes were taken from Cox and Bonham [15] and Tavard *et al.*,[16] respectively.

Spectroscopic mean amplitudes of vibration (l values) calculated by Cyvin and Cyvin [17] were used in the trial structures as well as for many of the distances throughout this analysis (*cf.* Table 1). Since no experimental data were available, assumed frequencies and a force field were constructed with the aid of those of chlorosulphuric acid [18] and methanol.[19]

The bond angles were tested over a wide range of values in the trial structures. However, angle O–C–H was fixed at 109°. The bond distances r(C–H) and r(O–C) were also set at 1.10 and 1.428 Å, respectively. The O · · · O distance was not varied in most of the refinements. The tetrahedral bond configuration around the sulphur atom yields closely grouped non-bonded distances; these distances and their vibrational amplitudes are strongly correlated. Since a remarkable constancy for r(O · · · O) was observed for a series of simple sulphones [4,7] at 2.48—2.49 Å, such a constraint [r(O · · · O) 2.485 Å] seemed to be reasonable. In the final stage of analysis, refinements were carried out with assumed values of 2.47 and 2.50 Å for r(O · · · O) to take account of the possible influence of this assumption and for a more realistic error estimate.

TABLE 1

Molecular parameters of methyl chlorosulphate

	Geometrical parameters [a]		Amplitudes of vibration		
		σ_T [b]	e.d.[c]	σ_T	s.c.[c]
(*a*) Independent distances (Å)					
C–H	[1.101] [d]		[0.079] [d]		0.079
O–C	[1.428] [d]		[0.049] [d]		0.049
S=O	1.419	0.003	0.040	0.002	0.035
S–O	1.562	0.004	[0.049] [d]		0.049
S–Cl	2.023	0.004	0.046	0.002	0.043
O · · · O (O=S=O)	[2.485] [d]		0.081 [e1]	0.006	0.056
(*b*) Independent angles (°)					
O–C–H	[109] [d]				
S–O–C	114.4	1.1			
Cl–S–O	102.8	1.4			
O–S=O	108.7	0.8			
C–O–S–Cl	74	4			
(*c*) Dependent distances (Å)					
(*i*) Independent of rotation					
O · · · O (O–S=O)	2.423	0.015	0.098 [e1]		0.074
Cl · · · O (Cl–S–O)	2.816	0.018	0.100 [e2]	0.005	0.105
S · · · C	2.514	0.011	0.089 [e1]		0.064
Cl · · · O(Cl–S=O)	2.779	0.009	0.065 [e2]		0.070
(*ii*) Rotation-dependent, *gauche*					
Cl · · · C	3.301	0.027	0.136	0.020	0.137
O · · · C(short)	2.750	0.022	0.100 [e2]		0.106
O · · · C (long)	3.710	0.015	0.063	0.026	0.072
(*iii*) Rotation-dependent, *anti*					
Cl · · · C	4.180	0.016	[0.094]		0.094
O · · · C	2.992	0.022	[0.100]		0.100
(*d*) Dependent angles (°)					
O=S=O	122.2	1.5			
O=S–Cl	106.4	0.6			

Amount of *gauche* form (%): α, 89 (σ, 8)

[a] All distances are r_a. [b] Total errors including least-squares standard deviations, experimental errors, and uncertainties originating from the assumption of r(O · · · O), see text. [c] e.d. = Electron diffraction; s.c. = spectroscopic calculations. [d] Not varied. [e] Refined in groups, *e*1 and *e*2, respectively.

The experimental data could be well approximated using a *gauche* conformer, in which the angle of rotation is *ca.* 74°. However, there was a slight feature at r *ca.* 4.10 Å in the experimental radial distribution which prompted us to examine the possible existence of the *anti* form. Another reason for looking carefully for the *anti* form was that both *gauche* and *anti* form were found to coexist in the vapour of methyl fluorosulphate in the electron-diffraction analysis,[9] and furthermore the *anti* form was found to prevail according to the microwave spectrum of $SFO_2(OMe)$.[9] Independently of the conditions of the refinements used, however, the amount of the *anti* form did not exceed 11%. The *syn* form, although thought to be unlikely for steric reasons, was also tested and ruled out by least-squares calculations.

The results of the refinements are collected in Table 1. The total errors, σ_T, include the standard deviations from the least-squares refinements multiplied by $3^{\frac{1}{2}}$ for data correlation and an estimated 0.2 and 2% experimental error for the distances and amplitudes, respectively. In addition, the errors were increased by adding the changes in the parameters that occurred when the assumed values of r(O · · · O) were changed to cover the interval 2.470—2.500 Å.

DISCUSSION

The bond lengths and bond angles, as well as the non-bonded distances characterizing the sulphur bond con-

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figurations in SO_2X_2, $SO_2X(OMe)$, and $MeSO_2X$ (X = F or Cl), are collected in Table 2. The variations in the bond lengths and bond angles as various ligands are attached to the sulphonyl group are consistent with the VSEPR model. Although the relatively large experimental errors may often conceal this, the observation certainly seems to be true for the relatively large series of sulphone molecules. Application of the VSEPR rules is further complicated by the presence of competing effects.[3] In addition to changes in the bond lengths and bond angles, the constancy of most of the non-bonded distances around the sulphur atom is noteworthy. This may be an indication of the importance of non-bonded interactions in establishing the actual sulphur bond configurations.

TABLE 2

Geometrical parameters for the sulphur bond configuration in some simple sulphones [a]

SO_2XY [b]	SO_2F_2						
	c	*d*	SO_2Cl_2 [e]	$SFO_2(OMe)$ [f]	$SClO_2(OMe)$ [g]	$MeSO_2F$ [h]	$MeSO_2Cl$ [i]
(*a*) Distances (Å)							
r(S–X)	1.530(3)	1.530(2)	2.011(4)	1.545(6)	2.023(4)	1.561(4)	2.046(4)
r(S=O)	1.405(3)	1.397(2)	1.404(4)	1.410(2)	1.419(4)	1.410(3)	1.424(3)
r(S–O)				1.558(7)	1.562(4)		
r(S–C)						1.759(6)	1.763(5)
r(O ··· X) [O=S–X]	2.379	2.378	2.781	2.373	2.779	2.378	2.816
r(O ··· O) [O=S=O]	2.481		2.485	2.491	[2.485]	2.480	2.477
r(O ··· Y) [O=S–Y]				2.424	2.423	2.604	2.610
r(X ··· Y)				2.317	2.816	2.512	2.945
(*b*) Angles (°)							
O=S–X	108.3	108.6(2)	107.7(4)	106.8(5)	106.4(6)	106.2(4)	107.1(7)
O=S=O	124.0(2)	122.6(12)	123.5(10)	124.4(7)	122.2(15)	123.1(15)	120.8(8)
O=S–Y				109.5(6)	108.7(8)	110.0	109.5
X–S–Y	96.1(2)	96.7(11)	100.0(7)	96.8(6)	102.8(15)	98.2(15)	101.0(14)

[a] Vapour-phase studies; r_a (electron diffraction) and r_0 (microwave spectroscopy) parameters; the uncertainties given in parentheses refer to the last significant figures and are taken directly from the original papers. [b] X = F or Cl; Y = F, Cl, O, or C. [c] Ref. 20. [d] Ref. 21. [e] Ref. 1. [f] Ref. 9. [g] Present study. [h] Ref. 3. [i] Ref. 2. The uncertainty in angle O=S=O was given as 3σ (2.4°) in the original paper; however, as a subsequent microwave spectroscopic study removed the ambiguity in this parameter, σ is given here similar to the other parameters.

The S–O–C bond angle in $SClO_2(OMe)$ is similar to that in $SFO_2(OMe)$ (116.5 ± 0.7°) [9] and intermediate between the C–O–C and S–O–S bond angles in OMe_2 (111.5 ± 1.5°) [22] and $O(O_2SF)_2$ (123.6 ± 0.5°).[23]

The relative abundance of the *gauche* conformer is certainly larger in the vapour of $SClO_2(OMe)$ than that in the vapour of $SFO_2(OMe)$.[9] On the basis of dipole-moment measurements, Exner *et al.*[24] concluded that the dihedral angle in $SClO_2(OMe)$ may have values from 0 to 60° and they excluded the *anti* form. Considering the uncertainty in the electron-diffraction determination of the dihedral angle and the inherent uncertainties in the dipole-moment calculations, the agreement is satisfactory.

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