

The Molecular Structure and Conformational Composition of Gaseous Methyl Chloroformate as Determined by Electron Diffraction

QUANG SHEN

Department of Chemistry, University of Trondheim, NLHT Rosenborg, N-7000 Trondheim, Norway

The molecular structure of methyl chloroformate has been studied at two different temperatures, 20 and 200 °C. Particular attention was paid to the conformational composition of the gaseous mixture. Both data sets are consistent with the presence of only the *syn* form. There is no evidence for the presence of the *anti* conformer, but models with 0% (15%) (20 °C) and 10% (20%) (200 °C) *anti* conformer cannot be ruled out by the electron diffraction experiment. For the *syn* form at 20 °C, the principal bond distances (r_a), and angles with error estimates of 2σ are: $r(\text{C}-\text{H})=1.092(24)$ Å, $r(\text{C}=\text{O})=1.190(4)$ Å, $r(\text{OC}-\text{O})=1.325(6)$ Å, $r(\text{O}-\text{CH}_3)=1.443(7)$ Å, $r(\text{C}-\text{Cl})=1.754(4)$ Å, $\angle \text{O}=\text{C}-\text{O}=128.1(6)^\circ$, $\angle \text{O}-\text{C}-\text{Cl}=108.7(4)^\circ$, $\angle \text{C}-\text{O}-\text{C}=114.4(17)^\circ$ and $\angle \text{H}-\text{C}-\text{O}=110.0^\circ$ (assumed).

The molecular conformation of methyl chloroformate has been the subject of considerable interest for a number of years.¹⁻⁹ Support for the existence of both *syn* and *anti* forms (Fig. 1) are discussed in a review by Jones and Owen.¹⁰ The only structural parameter values reported were by O'Gorman *et al.*² in an early electron diffraction study. During the course of our study, Durig and Griffin¹¹ reported the vibrational and the microwave spectra of gaseous methylchloroformate. In agreement with the earlier electron diffraction study, they concluded that the *syn* form was the prevailing conformer at room temperature, although small amounts of a second conformer could not be excluded. Due to various assumptions introduced, the uncertainties in the structural parameters were quite large. In order to supply accurate geometrical parameter values and to add information about the

possible presence of a second conformer, we shall report our electron diffraction studies of methyl chloroformate at 20 and 200 °C.

EXPERIMENTAL

The sample of methyl chloroformate (>97%, Merck) was checked by gas chromatography before use. The diffraction experiment was carried out at nozzle temperatures of 20 and 200 °C in the Oslo Balzers apparatus.¹² The experimental conditions are summarized in Table 1. The backgrounds were hand-drawn on the averaged curves from each of the two nozzle-to-plate distances. Before the averaging, the curves were plotted for visual check of uniformity.

STRUCTURE ANALYSIS

The structure analysis was carried out in the usual way.¹³ The atomic scattering and phase factors used were obtained from Schäfer, Yates and Bon-

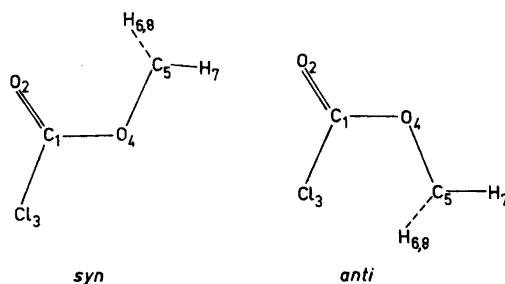


Fig. 1. Diagrams of the *syn* and *anti* forms of methyl chloroformate with atom numbering.

Table 1. Experimental conditions.

Nozzle temp. (°C)	20	200
Wave length (Å) ^a	0.05859	0.05859
Voltage (kV)	42	42
Bath temp. (°C)	0	0
Camera height (mm)	500.12	499.21
Plates used	4	4
s range (Å ⁻¹)	1.25–15.50	1.00–15.00
Δs	0.25	0.25
Camera height (mm)	250.12	249.27
Plates used	4	6
s range (Å ⁻¹)	6.00–29.00	7.50–26.50
Δs	0.25	0.25

^a Wave length calibrations were carried out by using benzene and TiCl₄ as standards.

ham's tables.¹⁴ Refinements of the structure were carried out by the method of least squares based on intensity curves by adjusting a single theoretical curve to the two average curves (one each from the long and short camera distances) using a unit weight matrix. The composites of these two experimental curves for 20 and 200 °C are shown in Fig. 2. The *syn* form of the molecule can be described by the following geometrical parameters: $r(\text{C}-\text{H})$, $r(\text{C}=\text{O})$, $\langle \text{C}-\text{O} \rangle = (r(\text{C}_1-\text{O}_4) + r(\text{C}_5-\text{O}_4))/2$,

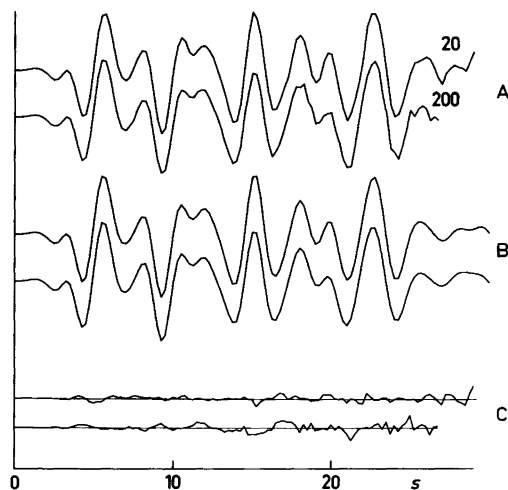


Fig. 2. Experimental (A), theoretical (B) and difference (C) intensity curves for methyl chloroformate at 20 and 200 °C. All curves are on the same scale and are in the form $sI_m(s)$ (see Ref. 13).

$\Delta(\text{C}-\text{O}) = r(\text{C}_5-\text{O}_4) - r(\text{C}_1-\text{O}_4)$, $r(\text{C}-\text{Cl})$, $\angle \text{O}=\text{C}-\text{O}$, $\angle \text{O}-\text{C}-\text{Cl}$, $\angle \text{C}-\text{O}-\text{C}$, $\angle \text{H}-\text{C}-\text{O}$ and τ (the $\text{H}-\text{C}-\text{O}-\text{C}$ torsional angle with zero taken as when one of the $\text{C}-\text{H}$ bond is eclipsing the C_1-O_4 bond). In all refinements $\angle \text{H}-\text{C}-\text{O} = 110.0$ and $\tau = 60.0^\circ$ were assumed.

NORMAL COORDINATE CALCULATION

The amplitudes of vibration were calculated¹⁵ using a valence force field similar to those reported for ethyl formate and ethyl chloroformate¹⁶ adjusted to fit the frequencies reported for methyl chloroformate.¹¹ However, the starting values for the $\text{OC}-\text{O}$ and $\text{O}-\text{CH}_3$ force constants used were the ones reported by Susi for methyl formate¹⁷ since Charles *et al.*¹⁶ have reservations about their values. Also these two $\text{C}-\text{O}$ distances are found to differ by 0.1 Å in both methyl formate^{18,19} and methyl chloroformate and are likely to have different force constants. The calculated potential energy distribution shows a rather complicated picture with substantial mixing between the different modes and hardly allows a straightforward assignment. The assignments in general agreed with the description given by Charles *et al.* for ethyl chloroformate.¹⁶ We felt that the force field is adequate for the calculation of amplitudes which are not too sensitive to the force field employed.

From the methoxy torsion force constant obtained from the analysis (fitting the 163 cm^{-1} frequency), values of δ (root mean square amplitude of torsion motion around the C_1-O_4 bond) were estimated to 14° at 20°C and 18° at 200°C . These δ values were used in the least square refinements.¹³ The calculated amplitudes were used whenever they are not refined in the least squares analyses. In cases where several amplitudes were refined as a group, their calculated differences were maintained. The same force field was used in calculating the amplitudes of vibration for the *anti* form.

CONFORMATION

The experimental radial distribution curves at both temperatures were found to be in good agreement with a model consisting of only the *syn* conformer. The RD-curves corresponding to the final model (100% *syn*) are shown in Fig. 3. If an *anti* conformer were present, the shape of the curve in

Table 2. Final results for methyl chloroformate at 20 and 200 °C.^a

	20 °C		200 °C	
	r_a	l^b	r_a	l
C—H	1.092(24)	0.078	1.092	0.078
$\langle C-O \rangle$	1.384(6)		1.395(8)	
$\Delta(C-O)$	0.117(8)		0.122(10)	
C—Cl	1.754(4)	0.044(5)	1.757(6)	0.047(6)
$\angle O=C-O$	128.1(0.6)		128.8(0.8)	
$\angle O-C-Cl$	108.7(0.4)		108.0(0.7)	
$\angle C-O-C$	114.4(1.7)		112.7(2.4)	
$\angle H-C-H$	110.0		110.0	
$\tau(H-C-O-C)$	60.0		60.0	
C=O	1.190(4)	0.042	1.188(7)	0.037
C—O	1.325(6)	0.050	1.334(8)	0.046
O—C	1.443(7)	0.055	1.457(10)	0.051
O ₂ ...Cl ₃	2.602(7)	0.057	2.604(11)	0.065
O ₄ ...Cl ₃	2.516(7)	0.059	2.513(10)	0.067
O ₂ ...O ₄	2.263(8)	0.053	2.276(12)	0.057
C ₁ ...C ₅	2.327(18)	0.071	2.324(32)	0.082
O ₄ ...H ₆	2.084(18)	0.107	2.098(8)	0.111
H ₆ ...H ₇	1.772(38)	0.127	1.777(8)	0.128
C ₅ ...Cl ₃	3.876(12)	0.074(14)	3.878(19)	0.078(14)
C ₅ ...O ₂	2.682(28)	0.104	2.675(50)	0.120
Cl ₃ ...H ₆	4.235(19)	0.161	4.230(32)	0.183
Cl ₃ ...H ₇	4.595(21)	0.112	4.609(15)	0.119
O ₂ ...H ₆	2.687(28)	0.347	2.657(64)	0.430
O ₂ ...H ₇	3.753(32)	0.121	3.750(46)	0.137
C ₁ ...H ₆	2.617(25)	0.189	2.609(41)	0.222
C ₁ ...H ₇	3.249(24)	0.103	3.255(22)	0.108
R ^c	0.100		0.122	

^a Distances (r_a) and amplitudes (l) in Ångströms; angles in degrees. Parenthesized values are 2σ and they include estimates of systematic uncertainties and correlations among the data. ^b Braced values were refined as a group. ^c $R = [\sum \Delta_i^2 / \sum I_i(\text{obs})^2]^{1/2}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{calc})$.

Table 3. Correlation matrix for methyl chloroformate 20 °C results.^a

Parameters	σ^b													
C—H	0.006	100												
C=O	0.001	15	100											
$\langle C-O \rangle$	0.001	15	15	100										
$\Delta(C-O)$	0.002	-38	-8	27	100									
C—Cl	0.001	-18	-32	-30	23	100								
$\angle O=C-O$	0.155	2	-4	-11	15	48	100							
$\angle O-C-Cl$	0.119	9	10	-40	-13	-14	-37	100						
$\angle C-O-C$	0.415	-17	-15	-38	-15	-2	-40	41	100					
l_{12}	0.002	39	11	14	-39	-25	-15	-12	10	100				
l_{13}	0.002	-31	9	19	29	-6	-13	-32	11	13	100			
l_{35}	0.005	-7	14	15	-1	-1	-35	-11	9	12	24	100		

^a Angles in degrees and distances in Ångströms. ^b Standard deviations from least squares.

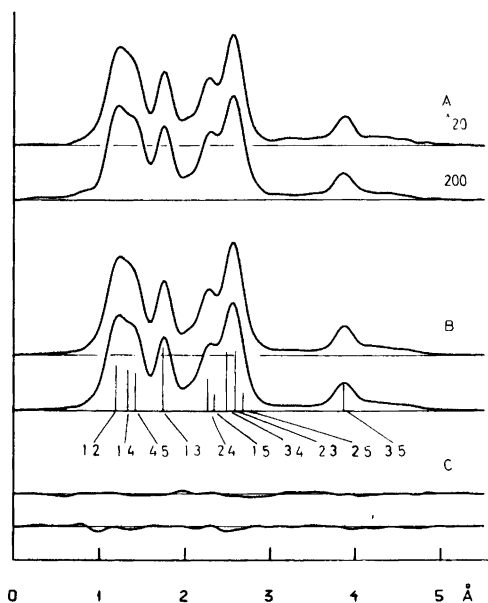


Fig. 3. Experimental (A), theoretical (B) and difference (C) radial distribution curves for methyl chloroformate at 20 and 200 °C. The lengths of the vertical bars are proportional to the weights of the distances.

the region $r > 3.0$ Å would be different due to the increase of the $O_2 \cdots C_5$ distance and the decrease in the $C_5 \cdots Cl_3$ distance.

The possible presence of an *anti* conformer (assumed to have the same structure as the *syn* conformer except for the $O=C-O-C$ torsion angle) was tested by refining the composition parameter simultaneously with other structural

parameters and values of 0% ($2\sigma = 15\%$) and 10% ($2\sigma = 20\%$) were obtained for the 20 and 200 °C data, respectively. The *R* factors (see Table 2) were virtually the same as those obtained assuming pure *syn* conformer. Radial distribution curves calculated with more *anti* conformer than the 2σ showed poorer agreement. There is no significant change in the gaseous composition between 20 and 200 °C. There is no evidence for the presence of significant amount of the *anti* in either set of data. Thus in the final refinements a model with pure *syn* was assumed for both temperatures. The final results are shown in Table 2 and the corresponding theoretical intensity and radial distribution curves are shown in Figs. 2 and 3. Table 3 is the correlation matrix for the results from the 20 °C experiment.

STRUCTURE

In Table 4 the values of the geometrical parameters obtained for methyl chloroformate from this, the microwave¹¹ and the earlier electron diffraction² investigations are shown together with those for methyl formate.¹⁹ The parameter values from these investigations are consistent within experimental errors except for the $OC-O$ bond where in the microwave work¹¹ for methyl chloroformate a rather large value of 1.36(2) Å was obtained. Judging from our results and the results obtained for methylformate [1.342(7) Å from ED¹⁹ and 1.334(10) Å from MW¹⁸] we felt that our value of 1.325(6) Å was a more reasonable one. Comparing the molecular structures of methyl formate and methyl chloroformate it is not surprising that both the $C=O$ and the $CO-O$ bonds are shorter in the latter since

Table 4. Bond lengths (Å) and angles (°) for methyl chloroformate and methyl formate.

	$ClCOOCH_3$	$ClCOOCH_3$	$ClCOOCH_3$	$HCOOCH_3$
C-H	1.092(24)	1.07(2)	—	1.081(20)
C=O	1.190(4)	1.19(2)	1.19(3)	1.206(5)
C-O	1.325(6)	1.36(2)	1.36(4)	1.342(7)
O-CH ₃	1.443(7)	1.43(2)	1.47(4)	1.445(4)
C-X	1.754(4)	1.73(2)	1.75(2)	1.101
$\angle O=C-O$	128.1(6)	125(2)	126(4)	126.8(1.6)
$\angle O-C-X$	108.7(4)	109(2)	111(4)	109.3
$\angle C-O-C$	114.4(1.7)	115(2)	112(3)	114.3(2.9)
$\phi(O=C-O-C)$	0 ^a	0	0-20	0
Method	E.D.	M.W.	E.D.	E.D.
Ref.	This work	11	2	18

^a Zero degree corresponding to *syn*.

substitution of a proton by a chlorine atom usually decreases the adjacent bond distances. The O-CH₃ bonds, however, remain unchanged. The O-C(sp²) and O-C(sp³) bonds in methyl formate¹⁹ [1.342(7) and 1.445(5) Å] are, respectively, shorter and longer than the corresponding ones in methylvinyl ether²⁰ [1.360(3) and 1.428(3) Å]. These changes may be attributed to the increased conjugation in the O-C(sp²) bond by lone pair participation and a consequential weakening of the O-C(sp³) bond caused by replacing the methylene group by a more electronegative oxygen atom. The C-Cl bond of 1.754(4) Å lies in between the C(sp²)-Cl bonds of 1.746(10) Å for phosgene²¹ and 1.798(2) Å for acetyl chloride.²²

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