Molecular Structure and Composition of Gaseous Methyl Formate as Determined by Electron Diffraction

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If one disregards the orientation of the methyl group, methyl formate can exist in two forms, *syn* and *anti* derived from rotation about the C1−O4 single bond (Fig. 1). The molecular structure has been studied at room temperature by electron diffraction[1] and microwave spectroscopy[2] and in both investigations no evidence for the presence of other than the *syn* form was found. The object of the present study at an elevated temperature of 200 °C was to look for the possible presence of a second conformer.

The sample of methyl formate (> 98 %; Fluka) was checked by gas chromatography before use. The diffraction experiment was carried out at a nozzle temperature of 200 °C in the Oslo Balzers apparatus,[3] with an electron wavelength of 0.05859 Å and nozzle-to-plate distances of 499.20 and 249.36 mm. Three plates from the long and four plates from the short distance were selected for analysis. Data covered the s ranges 1.25−15.25 (long distance) and 5.00−29.75 (short distance) in intervals $\Delta s = 0.25$. Smooth hand-drawn background curves were subtracted from the reduced data to yield intensity curves.

The structural analysis was carried out in the usual way.[4] Refinements of the structure were done by the method of least squares based on the two intensity curves in the form $sI_m(s)$ using a unit weight matrix. The geometrical parameters were $r(C=O)$, $r(C-H_m)$ ($H_m =$
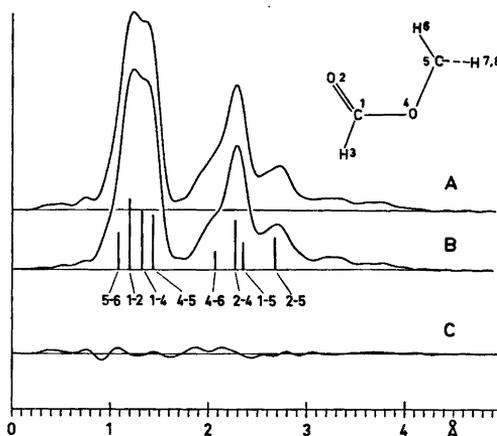

Fig. 1. Experimental (A), theoretical (B) and difference (C) radial distribution curves for methyl formate with $B = 0.0020$. The lengths of the vertical bars are proportional to the weights of the distances.

Table 1. Final results for methyl formate ^{a}.

Parameter	r_a	l	Parameter	θ/r_a	l
$C-H_m$	1.081(20)	0.077	$\angle O=C-O$	126.8(16)	
$C=O$	1.206(5)		$\angle O-C-H$	109.3	
$\langle C-O \rangle$	1.393(5)		$\angle C-O-C$	114.3(16)	
$\Delta C-O$	0.104(7)		$\angle O-C-H_m$	110.2(28)	
$C-H$	1.101	0.077	τ	60.0	
R^b	0.13		δ	0.0	
Other distances and amplitude parameters					
$C=O$	1.206(5)	0.027 ⎫	$C5\cdots O2$	2.683(23)	0.114(20)
$C1-O4$	1.341(7)	0.035 ⎬ (7)	$C5\cdots H3$	3.292(17)	0.104
$O4-C5$	1.445(5)	0.040 ⎭	$H3\cdots H6$	3.630(44)	0.193
$O2\cdots H3$	2.036(18)	0.090 ⎫	$H3\cdots H7$	4.074(32)	0.143
$O4\cdots H3$	1.997(6)	0.092 ⎬ (17)	$O2\cdots H6$	2.667(46)	0.38
$O4\cdots H5$	2.082(32)	0.103 ⎭	$O2\cdots H7$	3.748(28)	0.127
$O2\cdots O4$	2.279(10)	0.057 ⎫ (9)	$C1\cdots H6$	2.627(43)	0.219
$C1\cdots C5$	2.341(25)	0.076 ⎬	$C1\cdots H7$	3.259(30)	0.106
$H7\cdots H6$	1.758(54)	0.128 ⎭			

^{a} Distances (r_a) and amplitudes (l) in Å; angles in degrees. Bracketed values were refined as groups. Values in parentheses are 2σ. Values with no errors associated are not refined. ^{b} R = $[\Sigma w_i \Delta_i^2/\Sigma w_i I_i(obs)^2]^{\frac{1}{2}}$, where $\Delta_i = I_i(obs) - I_i(calc)$.

proton on the methyl group), $\langle C-O \rangle = (r_{14}+r_{45})/2$, $\Delta(C-O)=r_{45}-r_{14}$, $r(C-H)=1.101$ Å (assumed), $\angle C-O-C$, $\angle H_m-C-O$, $\tau(H_m-C-O-C)=60°$ (assumed, where $0°$ is as when a $C-H$ bond is eclipsed with $C1-O4$), and $\delta(O=C-O-C)=0.0$ (assumed, with $0°$ taken as planar *syn*). The above assumptions were taken from the microwave results [3] and were verified by test refinements. For example, $\tau=0.0$ gave worse agreement than $\tau=60°$, and a rough refined value for $\angle O-C-H$ was found to be $107\pm10°$.

From the appearance of the radial distribution curve (Fig. 1), it was clear that refinements of more than a few amplitudes of vibration were impossible. Accordingly amplitudes were calculated [5] from a rough force field similar to those reported for methyl formate [6] and ethyl formate [7] chosen to fit the reported frequencies.[8] These calculated amplitude values

were used whenever refinements were not feasible. In cases where several amplitude parameters were grouped together their differences as indicated by the calculated values were maintained. For details, see the final results of least squares refinement summarized in Table 1. The corresponding correlation matrix is given in Table 2.

The experimental radial distribution curve (Fig. 1) was found to be in good agreement with a model consisting of only the planar *syn* conformer. The radial distribution curve corresponding to the final model is also shown in Fig. 1. If an *anti* conformer were to be present in appreciable amounts the shape of the curve in the region $r\simeq2.7$ Å would be less prominent, and that in the region $r\simeq3.5$ Å more prominent due to conversion of the $O2\cdots C5$ distance from *syn* to *anti*. Calculations testing the allowable amount of an *anti* conformer led to a result

Table 2. Correlation matrix for the parameters of methyl formate [a,b]

r_1	r_2	r_3	r_4	$\angle 1$	$\angle 2$	$\angle 3$	l_{12}	l_{23}	l_{24}	l_{25}
100	69	50	-58	-53	22	-33	27	2	-41	-13
	100	68	-73	-74	34	-32	40	1	-44	-11
		100	-47	-71	24	-37	49	5	-38	-12
			100	61	-28	20	-59	16	32	8
				100	-69	50	-42	-5	71	6
					100	-25	14	-11	-70	-14
						100	-23	4	30	6
							100	32	-12	-5
								100	14	-6
									100	5
										100

[a] Distances (r_a) and mean amplitudes of vibration (l) in Å, angles in degrees. [b] Standard deviations from least squares are $r_1=C-H_m(0.0072)$, $r_2=C=O(0.0016)$, $r_3=\langle C-O \rangle(0.0016)$, $r_4=\Delta(C-O)$ (0.0024), $\angle 1=\angle O=C-O(0.567)$, $\angle 2=\angle C-O-C(0.586)$, $\angle 3=\angle O-C-H_m(1.008)$, $l_{12}(0.0022)$, $l_{23}(0.0059)$, $l_{24}(0.0031)$, $l_{25}(0.0069)$.

Table 3. Bond distances (Å) and angles (°) for methyl formate.

Parameter	E. D.	Microwave	E. D.
$C-H_m$	1.081(20)	1.086(15)	—
$C=O$	1.206(5)	1.200(10)	1.22(3)
$C1-O4$	1.341(7)	1.334(10)	1.37(4)
$C4-C5$	1.445(5)	1.437(10)	1.47(4)
$C-H$	1.101	1.101(10)	—
$\angle O=C-O$	126.8(1.6)	125.8(1.0)	123(4)
$\angle O-C-H$	109.3	109.3(1.0)	—
$\angle C-O-C$	114.3(1.6)	114.8(1.0)	112(4)
$\angle O-C-H_m$	110.2(2.8)	108	—
τ	60.0	60.0	
δ	0	0	0−20
Ref.	This work	2	1

of $0-15$ %. The theoretical radial distribution curve corresponding to 15 % *anti* conformer was also found to be in poorer agreement with the experimental one than the curve for a model based on only the *syn* conformer. We concluded that there is no evidence for the presence of a second conformer.

The results from our present study compared very well with the earlier electron diffraction [1] and microwave [2] works (see Table 3). Comparison with the recent electron diffraction work on dimethyl carbonate ($CH_3OCOOCH_3$)[9] showed no substantial difference between values of comparable parameters. In both the formate and carbonate only comparable conformers *syn* and *syn-syn* were found.

It is of interest to compare two structurally related molecules like methyl formate and methylvinyl ether.[10] The $C(sp^2)-O$ bond is longer by 0.02 Å in the ether than in the formate and the $C-O-C$ value is 4° greater in the ether. Also, in contrast to methyl formate, two conformers (73 % *syn* and 27 % *anti*) are observed for methylvinyl ether at 210 °C. Assuming that the entropy differences of conformers are similar, these results are in agreement with the *ab initio* molecular orbital calculations [11] showing the *anti* form to be $4-8$ kcal mol^{-1} above the *syn* form in methyl formate while the *anti* form is only $1-2$ kcal mol^{-1} above the *syn* form in methylvinyl ether (1 kcal = 4.184 kJ).

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The Coefficients for Isothermal Transport. II. Cation Exchange Membrane and Electrodes Reversible to One of the Cations

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A rigorous thermodynamic description of electrolyte transport across a membrane has been given in a previous publication by Førland, Førland and Ratkje.[1] Specific for their presentation is that the number and kind of components used to describe the system, conform with the phase rule. The presentation deals only with measurable quantities. This ensures an independent choice of forces in the flux equations.

When restrictions such as selectivity of the membrane and of the electrodes are imposed on the mass and charge transfer, relations between the phenomenological coefficients of the flux-force system may be developed.[1,2] Relations were obtained for anion electrodes and a cation selective membrane.[1] This communication is a supplement to the previous work. The effect of substituting anion electrodes by cation electrodes is investigated. Information of the relative size of the phenomenological coefficients is developed.

Transports in an ion exchange membrane placed between electrodes reversible to a cation. The number of mass fluxes in a transport system of n components is $(n-1)$, the flux of the n'th component being chosen as the zero reference.[1] With an electric current passing through the system there are independent forces. In the Førland-Ratkje formalism these are the $(n-1)$ gradients in chemical potential and the gradient in electric potential.[1] The fluxes J_i are linear combinations of the forces X_j:

$$J_i = \sum_{j=1}^{n} L_{ij}X_j \tag{1}$$

When the fluxes are linearly dependent

$$\sum_{i=1}^{n} \alpha_i J_i = 0 \tag{2}$$

general relations between the phenomenological coefficients have been developed.[1,2]

$$\sum_{i=1}^{n} \alpha_i L_{ij} = 0 \quad j = 1,...,n \tag{3}$$

α_i, $i=1,...,n$, are coefficients giving the interdependency.