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2-Methoxypropene. Gas Phase Molecular Structure and Conformation as Determined by Electron Diffraction

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At room temperature gaseous 2-methoxypropene exists essentially as one conformer, the form where the O–CH_3 bond eclipses the carbon–carbon double bond. However, amounts of *ca.* 10 % of a second conformer cannot be excluded. The structural results in terms of r_a distances and $\angle_\alpha$ angles are as follows: r(C=C) = 1.330(7)Å, r(C–C) = 1.501(8)Å, r(=C–O) = 1.353(5)Å, r(O–CH_3) = 1.416(5)Å, ∠C=C–C = 123.9(8)°, ∠C=C–O = 125.8(7)°, ∠C–O–C = 116.0(1.1)°, ∠C=C–H = 121.4(3.9)°, ∠C–C–H = 112.1(2.7)°, ∠O–C–H = 109.7(1.7)°, *syn* torsional amplitude is 11.9(2.6)°. Error estimates are given as 2σ, where σ includes uncertainties due to correlation among observations, electron, wavelength and other parameters used in the data reduction.

Methyl vinyl ether, which is closely related to 2-methoxypropene, has been thoroughly investigated during the last decade. It is well established, both by theoretical [1–4] and experimental [5–12] methods, that the predominant conformer is the one with the O–CH_3 bond eclipsing the carbon–carbon double bond(τ=0°). The nature of the second conformer has been more questionable. However, the latest investigations point toward a second conformer with a planar skeleton.[1–3,6,11,12]

According to the observations made for methyl vinyl ether, 2-methoxypropene was expected to exist mainly as a *syn* conformer, τ=0°. For sterical reasons a possible planar second conformer may seem less likely in this case. An infrared vibrational spectroscopic study of 2-methoxypropene [13] concluded that two conformers coexisted both in liquid and vapour phases, the most abundant one being *syn*. The energy difference in liquid phase was estimated to 3.5 kJ mol^{-1}. However, it could not be determined whether the second conformer was one with a planar skeleton or not. The conformational energy difference as obtained from the infrared spectra [13] indicates a contribution of 15–20 % of the less abundant conformer, which was expected to be detectable from an ED study. No structural study of 2-methoxypropene seems to exist.

EXPERIMENTAL AND DATA REDUCTION

The sample of 2-methoxypropene used for ED recordings was synthesized by A. O. Diallo as described in Ref. 13. It was distilled just before use and the purity was found to be 99 % from a gas chromatography test. Data were recorded with the Balzers Eldigraph KDG-2 apparatus [14,15] at a nozzle temperature of 20 °C. Nozzle-to-plate distances of 50 and 25 cm were used. The electron wavelength was calibrated against benzene. [16]. The electron diffraction photographs were recorded on Kodak Electron Image plates. Optical densities were measured with a Joyce Loebl densitomer. For the 50 and 25 cm data, 4 and 3 plates, respectively, were selected for analysis.

The data were reduced in the standard way, [17–18] giving two average experimental intensity curves in the form $sI_m(s)$, one for each camera distance. For calculation of electron scattering amplitudes and phase shifts, Hartree-Fock potentials [19] for C and O were used, while molecular bonded potentials were used for H.[20]

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NORMAL COORDINATE CALCULATION

The present structural study involves a molecule of low symmetry and a possibility for more than one conformer. Therefore, it was important to calculate the vibrational quantities as accurately as possible. A valence force field was used. This force field consists of a combination of force constants from valence force field of methyl vinyl ether[21] and isobutene. A similar transference of force constants have been made for compounds of the type $CH_2=C(CH_3)-CH_2X$, X=Cl, Br, CN.[22] Those calculations reproduced the observed frequencies satisfactorily. A similar calculation for 2-methoxy-propene was expected to reproduce observed frequencies[13] quite accurately. Unfortunately, torsional frequencies, which will be the most uncertain part of such a calculation, are not observed. Therefore, vibrational quantities were calculated for a wide range of torsional force constants, varying from 0.12 (as in 1-butene) to 0.38 mdyn Å $(rad)^{-2}$ (as in methyl vinyl ether). The valence force constants of the *syn* conformer are listed in Table 1. In Table 2, root mean square amplitudes of vibration (*l*) are given, corresponding to a torsional force constant 0.20 mdyn Å $(rad)^{-2}$.

The frequencies thus calculated deviate from the observed ones[13] by an average of 12 cm^{-1}. The calculation agrees well with the interpretation given in Ref. 13, with one important exception. The symmetric C–O–C stretch frequency was calculated to 828 cm^{-1}. This suggested that the band observed at 830 cm^{-1} may not solely be due to a second conformer. If so should be the case, the relative conformational energy difference may be considerably different from 3.5 kJ mol^{-1}, which was estimated from temperature effects on the 830 and 800 cm^{-1} bands in the vibrational spectra.[13]

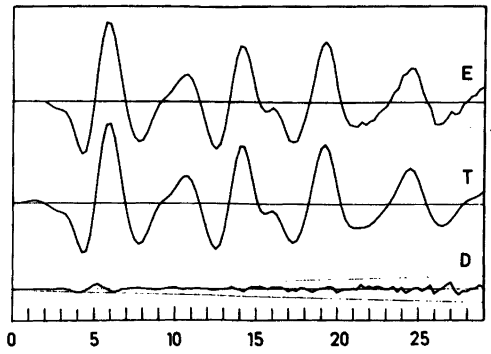

Fig. 1. 2-Methoxy-propene; intensity curves in the form $sI_m(s)$. Experimental curve (E) is the composite curve for all plates and camera distances. Theoretical curve (T) was calculated from parameters in Tables 2 and 3. Difference curve (D) is E–T. The straight lines show the experimental uncertainties as three times standard deviation. All curves are on the same scale. Δs=0.25 $Å^{-1}$.

STRUCTURAL ANALYSIS

The least squares refinements were based on intensity curves in the form $sI_m(s)$. The compo-

Table 1. 2-Methoxypropene; valence force constants in units of mdyn $Å^{-1}$ and mdyn Å $(rad)^{-2}$.

	Involved coordinate	Value	Involved coordinate(s)	Value	Involved coordinate(s)	Value
str.	C=C	9.14	$H-C_1-H$	0.35	$=C-O/O-CH_3$	0.28
	C–C	4.25	C–C–H	0.64	C_3-H/C_3-H	0.05
	=C–O	5.10	$H-C_3-H$	0.54	C_4-H/C_4-H	0.05
	$O-CH_3$	5.11	O–C–H	0.89	str/bend C=C/C=C–H	0.41
	=C–H	5.15	$H-C_4-H$	0.53	C=C/O–C–C	−0.43
	C_3-H	4.71	tors. C=C	0.49	C–C/O–C–C	0.32
	C_4-H	4.71	C–C	0.08	=C–O/O–C–C	0.32
bend	C=C–C	0.98	=C–O	0.20	C–C/C–C–H	0.38
	C=C–O	1.27	$O-CH_3$	0.08	$O-CH_3/O-C-H$	0.43
	O–C–C	0.73	o.o.p. CH_2	0.16	bend/bend C=C–O/C–O–C	0.46
	C–O–C	1.68	CC_2	0.35	C–C–H/C–C–H	−0.02
	C=C–H	0.52	str/str. =C–O/C–C	0.78	O–C–H/O–C–H	−0.04

Table 2. 2-Methoxy-propene; r_a distances and calculated root mean square amplitudes of vibration in Å.

Distance	r_a	l
=C–H	1.09	0.077
–C–H	1.10	0.079
C=C	1.33	0.042
=C–O	1.35	0.047
O–C_4	1.42	0.048
C–C	1.50	0.052
O···C_1	2.38	0.060
O···C_3	2.34	0.066
C_2···C_4	2.34	0.068
C_1···C_3	2.50	0.066
C_1···C_4	2.76	0.092
C_3···C_4	3.64	0.071

site experimental $sI_m(s)$ curve is shown in Fig. 1. A unit weight matrix was used. The molecular geometry was calculated using geometry consistent r_a parameters.[23]

Because of the low molecular symmetry, some constraints had to be made on the geometry parameters. Thus, both C=C–H angles were assumed to be equal. Both CH_3 groups were restricted to C_{3v} symmetry, with symmetry axis coinciding with the C–C and O–CH_3 bonds; one C–H bond in each methyl group was positioned *anti* to the =C–O bond. The difference Δr(C–H) = r(–C–H)–r(=C–H) was given an assumed value. Most of these geometrical parameters involving C–H, were difficult to refine together with the skeletal parameters. Therefore, their values were obtained from least squares refinements including fewer skeletal parameters than the final calculations (Table 3). For the calculations involving a second conformer, only the torsional angle τ (torsion around the =C–O bond) differed from the *syn* conformer value.

Along with the *syn* conformer, possible second conformers having different values for τ were included in refinements. In no case was the result more than 3±6 % contribution from the second conformer. Using vibrational quantity values calculated by the use of different torsional force constants had hardly any influence on the conformational composition.

Table 3. 2-Methoxy-propene; final structural results obtained from analysis of electron diffraction data at 20 °C (in Å and degrees, R in %).

Parameter No.	Parameter type	Parameter value (r_a, $\angle_a$)
1	r(C=C)	1.330(7)[a]
2	r(C–C)	1.501(8)
3	r(=C–O)	1.353(5)
4	r(O–CH_3)	1.416(5)
5	r(=C–H)	1.087(5)[b]
6	Δr(C–H)	0.015[c]
7	∠C=C–C	123.9(.8)
8	∠C=C–O	125.8(.7)
9	∠C–O–C	116.0(1.1)
10	∠C=C–H	121.4(3.9)[b]
11	∠C–C–H	112.1(2.7)[b]
12	∠O–C–H	109.7(1.7)
13	$\langle \tau_s^2 \rangle^{1/2}$	11.9(2.6)
	R	6.7

[a] Systematically varied, uncertainty estimated. [b] Value not obtained from final refinement, see text. [c] Assumed value.

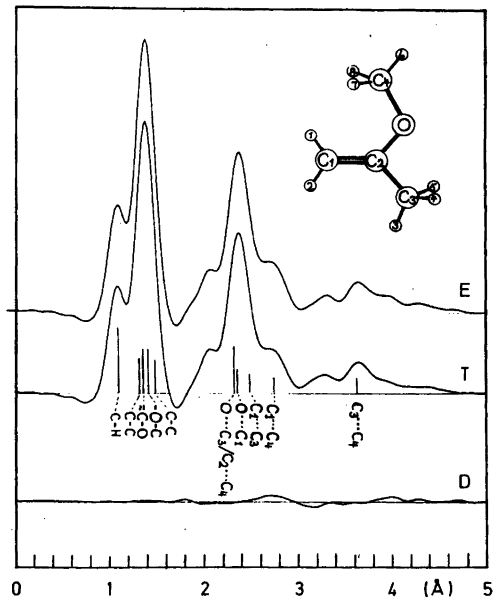

Fig. 2. 2-Methoxy-propene; radial distribution curves as Fourier transforms of the intensity curves in Fig. 1, using B=0.0020 Å, and theoretical data for unobserved area $0<s<2.25$. The vertical lines show the most important distances, height being proportional to weight of distance. All curves are on the same scale. In the atomic numbering figure, hydrogens are denoted by numbers only.

Table 4. 2-Methoxypropene; correlation matrix corresponding to the final refinement. Numbering of parameters is given in Table 3. σ_o is standard deviation obtained from least squares calculation.

No.	2	3	4	7	8	9	12	13
3	.36							
4	.12	−.36						
7	.10	.29	−.06					
8	.23	−.10	.23	−.61				
9	−.24	−.11	−.17	−.75	−.55			
12	−.20	.03	−.25	−.03	−.15	.18		
13	.03	−.11	.15	−.28	.08	−.39	−.36	
1	−.56	−.98	.88	−.88	−.06	−.21	−.39	.09
σ_o	.002	.001	.001	.3	.3	.4	.6	.9

In the final refinement, only one conformer was considered. All vibrational quantities were kept at their calculated values given in Table 2. All four bonded skeletal distances are located in the same peak in the radial distribution (RD) curve, separated by only 0.17 Å. Likewise, the four C···X (X=C,O) distances over one angle are closely positioned in the RD curve, differing by only 0.16 Å. Thus, there were large correlations among several of the parameters (Table 4). Therefore, the C=C distance was determined by a systematic variation, while all other skeletal geometrical parameters were refined.

RESULTS AND DISCUSSION

The geometry parameters as obtained from the final refinements are given in Table 3. The error estimates are 2σ, where σ includes correction for correlation among observations and uncertainties in wavelength and other parameters used in the data reduction.[18] The correlation matrix is given in Table 4. The corresponding theoretical intensity curve can be found in Fig. 1, while the RD curves are shown in Fig. 2.

It was found that gasous 2-methoxypropene consists of practically only one conformer. No significant evidence of a second form was found but amounts of up to 10 % of a second form could not be excluded. The essentially one-conformer result does not agree well with the conformational result from vibrational spectroscopy.[13] However, a reinterpretation of the observed frequencies as suggested from the normal coordinate analysis, would change the result anyway.

In Table 5 some of the geometrical parameters of 2-methoxypropene are compared with those of related molecules. Relative to methyl vinyl ether, the C=C–O angle is smaller. This was expected, since the neighbouring C=C–C angle is more resistant to decrease than a C=C–H angle. A similar trend is observed when comparing 1-butene[24] with 2-methyl-1-butene.[25] Then the =C–C–C angle increases as the C=C–C angle decreases. That the corresponding C–O–C angle in 2-methoxypropene decreases compared to the observed value in methyl vinyl ether,[6] may be due to the interaction between the lone pairs of oxygen and the 2-methyl group. Compared to the aliphatic ethers,[26–28] the C–O–C angle in 2-methoxypropene is still considerably larger.

The slight misfits observed at a few locations in the RD curve could have been smoothed out by refining some vibrational amplitudes. However, as so many carbon–carbon and carbon–oxygen distances are located closely together, it was considered better to use calculated values for vibrational quantities throughout the analysis.

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Table 5. Comparison of geometrical parameters for molecules related to 2-methoxypropene.

Molecule	r(C–O)	r(O–CH_3)	r(C–C)	r(C=C)	C=C–O	C–O–C	Ref.
CH_2=C(CH_3)–O–CH_3(ED)	1.353(5)[a]	1.416(5)	1.501(8)	1.330(7)	125.8(.7)	116.0(1.1)	This work
CH_2=CH–O–CH_3(ED)	1.360(3)	1.428(3)	–	1.341	127.7(1.4)	118.3(1.1)	6
CH_2=C=CH–O–CH_3(ED)	1.375(7)	1.427(8)	–	–	125.3(1.2)	115.0(1.2)	30
CH_3–O–CH_3(ED)	–	1.416(3)	–	–	–	111.5(1.5)	27
CH_3–O–CH_2–CH_3(ED+MW)	–	1.413(9)	–	–	–	111.9(.5)	26
CH_3–O–CH_2–O–CH_3(ED)	–	1.432(4)	–	–	–	114.6(.5)	28
Ph–O–CH_3(ED)	1.361(15)	1.423(15)	–	–	–	120(2.0)	29
CH_2=C(CH_3)–CH_2CH_3(ED)	–	–	1.515	1.334	[125.2][b]	[116.0][b]	25
CH_2=CH–CH_2–CH_3(ED+MW)	–	–	1.502(2)	1.340(4)	[127.2(3)][b]	[114.9(.3)][b]	24

[a] Uncertainties are not comparable throughout the table. [b] C=C–C and C–C–C angles.

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