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2-BROMO-3-CHLORO-1-PROPENE: GAS PHASE MOLECULAR STRUCTURE AND CONFORMATIONAL COMPOSITION AS DETERMINED BY ELECTRON DIFFRACTION

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ABSTRACT

The molecular structure and conformational composition of 2-bromo-3-chloro-1-propene have been determined by gas-phase electron diffraction at nozzle temperatures of 20, 90 and 187°C. There is a mixture of two conformers in the gas phase with the halogen atoms *anti* or *gauche* to each other. The *anti* conformer (torsion angle τ = 0) is the most stable with 48(11), 45(9) and 38(9)% at 20, 90 and 187°C, respectively. This corresponds to an energy difference (with standard deviation) of $\Delta E = E_g - E_a = 3 \pm 1$ kJ mol^{-1}, and an entropy difference $\Delta S = 4 \pm 3$ J mol^{-1} K^{-1}. The geometry of the molecule at 20°C is described by the following r_a and $\angle_\alpha$ parameters (error limits are 2σ including corrections for correlation among observations and other experimental uncertainties): $r(C=C) = 1.360(14)$ Å, $r(C—C) = 1.491(16)$ Å, $r(C—Br) = 1.911(11)$ Å, $r(C—Cl) = 1.803(9)$ Å, $\langle r(C—H)\rangle = 1.139(30)$ Å (average C—H distance), $\angle C=C—C$ (*anti*) $= 128.4(1.0)°$, $\angle C=C—Br$ (*anti*) $= 121.3(3.0)°$, $\angle C—C—Cl$ (*anti*) $= 113.0(2.6)°$, $\langle \angle C—C—H\rangle = 112.8(4.2)°$, τ (*gauche* torsional angle) $= 109.5(3.5)°$ and $\langle(\Delta\tau)^2\rangle^{1/2} = 10.6(3.6)°$ (r.m.s. torsional amplitude for the *anti* form). The difference between bond angles in the *anti* and *gauche* forms were estimated by molecular mechanics calculations and kept constant at the values $\Delta\angle C=C—C = \angle C=C—C$ (*anti*) $— \angle C=C—C$ (*gauche*) $= 2.4°$, $\Delta\angle C=C—Br = —0.8°$ and $\Delta\angle C—C—Cl = 0.7°$.

INTRODUCTION

The gas phase electron diffraction (ED) study of 2-bromo-3-chloro-1-propene (hereafter denoted BCP) was undertaken as a result of two lines of structural interest. Several haloacetyl halides have been found to exist as a mixture of two conformers [1—3] with the halogen atoms *anti* or *gauche* to each other. An ED study of 2,3-dichloro-1-propene (DCP) [4] showed the same type of conformational composition. Thus, this work is an extension of the study of structural differences resulting from the exchange of a carbon—oxygen double bond for a carbon—carbon double bond. Further, changes in the rotational conformational behaviour within

the fragment C=C—C—Cl, when different substituents are linked to the carbon skeleton, are currently being investigated by ED [5].

BCP has been studied by vibrational spectroscopy [6—8], which revealed that two conformers are present in considerable amounts. An IR solvent effect study [6] showed the two forms to be nearly equally abundant in the liquid phase. A rough visual study of the gas phase vibrational spectra [8], indicates a similar relationship in the gas phase.

EXPERIMENTAL AND DATA REDUCTION

BCP was a commercial sample from K and K with purity better than 95%. ED data were recorded with the Balzers Eldigraph KDG-2 [9, 10] at nozzle temperatures of 20, 90 and 187°C. Nozzle-to-plate distances of 50 and 25 cm were used. ED photographs were recorded on Kodak Electron Image plates. The electron wavelength was calibrated against benzene [11]. Optical densities were measured by a Joyce Loebl micro-densitometer for the 20°C data and by a single beam densitometer for the other data. From camera distances of 50(25) cm; 4(4), 5(5) and 5(4) plates were selected for analysis for the 20, 90 and 187°C data, respectively. The data were reduced in the usual way [12]. A calculated background [13] was subtracted from the data for each plate, yielding results in the form $I_m(s)$ [14]. Data from each camera distance were combined to one average curve. Electron scattering amplitudes and phase shifts were calculated analytically by a program originally written by Yates [15a]. For these calculations Hartree—Fock potentials [15b] were used for C, Cl and Br; while molecular bonded potentials were used for H [16].

Experimental intensity curves in the form $sI_m(s)$ are shown in Fig. 1. Experimental intensity data are available as a supplementary publication [17].

STRUCTURE ANALYSIS

The experimental radial distribution (RD) curves are shown in Fig. 2. The expected Br···Cl distances for *anti* and *gauche* conformers are located at 4.5 and 3.5 Å respectively. From Fig. 2 it is obvious that there are only minor changes in the conformational composition as the temperature is increased.

Refinements of the structure were based on intensity curves in the form of $sI_m(s)$, using a unit weight matrix in the least square calculations.

Preliminary calculations of RD-curves showed the molecules to be a mixture of *anti* and *gauche* conformers. The amount of steric strain is expected to be different in the *anti* conformer compared to the *gauche*. Therefore, the angles C=C—C, C=C—Br and C—C—Cl were allowed to have different values in the two conformers. For some molecules of the type CH$_2$=CH—CH$_2$X there seems to be experimental support for larger C=C—C and C—C—X angles
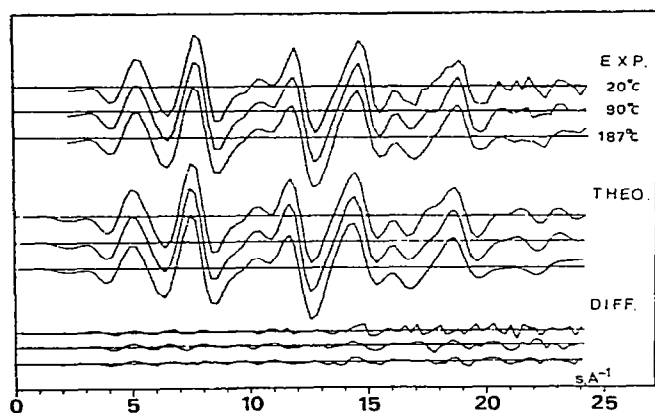
Fig. 1. 2-Bromo-3-chloro-1-propene. Intensity curves in the form $sI_m(s)$. Experimental curves are the composite curves for all plates. Theoretical curves were calculated from parameter values in Tables 1 and 2. Difference curves are experimental minus theoretical. All curves are on the same scale and $\Delta s = 0.25$ Å^{-1}.
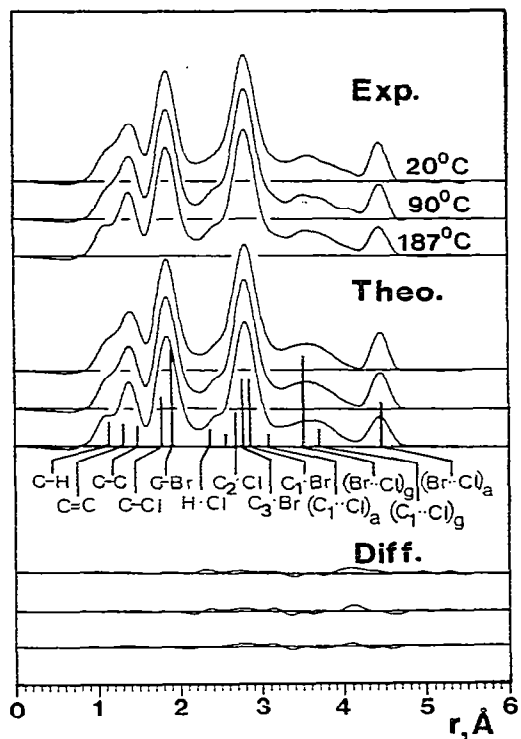

Fig. 2. 2-Bromo-3-chloro-1-propene. Radial distribution curves are calculated from the intensity curves of Figure 1 after multiplication by $Z_C Z_{Cl}/(f_C(s)f_{Cl}(s))$, using theoretical data for unobserved area $s < 2.0$ and with $B = 0.002$ Å^2. The vertical lines show the most important distances. All curves are on the same scale.

when the C—X bond is eclipsing the double bond [18—20]. This trend has been nicely reproduced by molecular mechanics (MM) calculations [21, 22]. Therefore, in the case of BCP the difference between *anti* and *gauche* bond angles ($\Delta(\angle C{=}C{-}C)$, $\Delta(\angle C{=}C{-}Br)$ and $\Delta(\angle C{-}C{-}Cl)$); were estimated from MM calculations of 2,3-dichloro- and 2,3-dibromo-1-propene [22]. The values obtained are given in Table 1. Such conformational structural differences gave a slight improvement in the R factor compared to use of conformationally averaged values.

All C—H distances were refined as an average value. The C=C—H angles were assumed to be equal and the CH_2Cl group was assumed to have C_s symmetry. Root mean square amplitudes of vibration (l) and perpendicular correction coefficients (K) were calculated from a valence force field given elsewhere [23]. The calculated vibrational amplitudes are listed in Table 2.

A good fit between calculated and observed intensity data was obtained

TABLE 1

2-Bromo-3-chloro-1-propene: final structural results (bond lengths in Å, bond angles in degrees and conformational composition in %; error-limits are 2σ)

No.	Parameter[a]	Value (r_a, $\angle_\alpha$)		
		20°C	90°C	187°C
1	$r(C{=}C)$	1.360(14)	1.350(15)	1.360(18)
2	$r(C{-}C)$	1.491(16)	1.467(13)	1.454(12)
3	$r(C{-}Br)$	1.911(11)	1.914(10)	1.912(10)
4	$r(C{-}Cl)$	1.803(9)	1.806(14)	1.804(17)
5	$\langle r(C{-}H)\rangle$	1.139(30)	1.142(24)	1.113(21)
6	$\angle C{=}C{-}C_g$	126.0(1.0)	125.6(1.2)	124.8(1.0)
7	$\Delta C{=}C{-}C$	2.4[b]	2.4[b]	2.4[b]
8	$\angle C{=}C{-}Br_g$	122.1(3.0)	121.3(3.9)	122.8(3.4)
9	$\Delta\angle C{=}C{-}Br$	−0.8[b]	−0.8[b]	−0.8[b]
10	$\angle C{-}C{-}Cl_g$	112.3(2.6)	113.3(3.7)	114.4(2 2)
11	$\Delta\angle C{-}C{-}Cl$	0.7[b]	0.7[b]	0.7[b]
12	$\angle C{=}C{-}H$	120.7(6.9)	120.7[c]	120.7[c]
13	$\angle C{-}C{-}H$	112.8(4.2)	112.8[c]	112.8[c]
14	$\angle C{-}Cl, C{-}H^d$	119.5(6.3)	119.5[c]	119.5[c]
15	τ_g^e	109.4(2.6)	111.2(2.9)	110.6(3.2)
16	$\langle(\Delta\tau)^2\rangle^{1/2 f}$	10.6(3.6)	11.7[c]	13.2[c]
17	α_a	48(11)	45(9)	38(9)
	R	12.4	9.9	9.1

[a]Subscripts g and a denotes *gauche* and *anti* respectively, Δ angle values are *anti* value minus *gauche* value. [b]Estimated from molecular mechanics calculations. [c]Value taken from 20°C data and corrected for temperature effects. [d]Angle between projections of C—Cl and —C—H bonds on plane perpendicular to C—C bond. [e]Torsional angle of *gauche* form relative to 0° for the planar *anti* form. [f]Root mean square amplitude of torsion for the *anti* conformer, assuming harmonic torsional motion around $\tau = 0$ and obtained using a dynamic model for the *anti* conformer [14].

TABLE 2

2-Bromo-3-chloro-1-propene; interatomic distances (r_a) and calculated and refined root mean square amplitudes of vibration, given as *gauche/anti* in units of Å

Distance		20°C		90°C		187°C	
Type	Value[a]	$l_{calc.}$	$l_{ref.}$	$l_{calc.}$	$l_{ref.}$	$l_{calc.}$	$l_{ref.}$
C–H	1.139	0.077	0.076(23)	0.077	0.077(20)	0.077	0.078(14)
C=C	1.360	0.042		0.043		0.043	
C–C	1.491	0.049	0.046(26)	0.049	0.037(27)	0.050	0.045(27)
C–Cl	1.803	0.052	0.062(20)	0.054	0.062(16)	0.057	0.067(14)
C–Br	1.911	0.057	0.062(24)	0.060	0.063(20)	0.065	0.070(19)
Br···Cl	3.49/4.46	0.173/0.071	0.187(11)/0.074(10)	0.192/0.078	0.198(18)/0.075(8)	0.215/0.086	0.213(18)/0.086(9)
Br···C$_1$	2.87	0.062/0.072	0.068/0.078 } (11)	0.066/0.077	0.064/0.075 } (10)	0.071/0.085	0.059/0.073 } (4)
Br···C$_3$	2.83	0.074/0.063	0.080/0.069	0.079/0.067	0.078/0.066	0.087/0.073	0.089/0.075
Cl···C$_1$	3.73/3.10	0.118/0.095	— /0.113(48)	0.129/0.103	— /0.097(25)	0.144/0.114	— /0.113(37)
Cl···C$_2$	2.73	0.077		0.083		0.091	
C$_1$···C$_3$	2.54	0.063		0.066		0.070	
Br···H$_1$	3.92	0.099		0.099		0.103	
Br···H$_2$	3.02	0.147		0.152		0.161	
Br···H$_4$	3.85/3.04	0.105/0.184		0.109/0.197		0.114/0.214	
Br···H$_3$	3.02/3.04	0.162/0.184		0.170/0.197		0.182/0.214	
Cl···H$_1$	3.99/2.71	0.205/0.169		0.220/0.173		0.240/0.190	
Cl···H$_2$	4.64/4.22	0.151/0.120		0.161/0.127		0.175/0.136	
Cl···H$_3$	2.38	0.116		0.118		0.121	
C$_1$···H$_4$	2.74/3.26	0.189/0.136		0.143/0.141		0.149/0.150	
C$_1$···H$_3$	3.35	0.117/0.136		0.119/0.141		0.124/0.150	
C$_2$···H$_1$	2.17	0.100		0.100		0.102	
C$_2$···H$_3$	2.19	0.104		0.105		0.106	
C$_3$···H$_1$	2.82	0.146		0.146		0.153	
C$_3$···H$_2$	3.56	0.100		0.101		0.103	

[a] *Gauche–anti* differences of less than 0.02 Å are not listed.

when all vibrational amplitudes were kept at their calculated values. During such a refinement all parameters except $\angle C=C-H$, $\angle C-C-H$, $\angle Cl-C-H$ and $\langle(\Delta\tau)^2\rangle^{1/2}$ could be varied simultaneously. As it was more difficult to obtain good convergence in the least squares refinements of the 90°C and 187°C data than for the 20°C data, some of the parameter values obtained from the 20°C experiments were used as constants in the two high temperature refinements.

RESULTS AND DISCUSSION

The results obtained from the analysis of the BCP data are listed in Table 1. The uncertainties are given as 2σ where σ includes corrections for correlation among observations and uncertainties in the electron wavelength and in the distance between photographic plate and scattering point. The correlation matrix for the 20°C experiment is given in Table 3. Intensity and RD curves for the various temperatures are shown in Figs. 1 and 2, respectively.

The carbon—carbon single bond showed an unexpectedly large variation with temperature. Since $r(C-Br)$ and $r(C-Cl)$ are very nearly constant, this variation cannot be a result of scale factor errors. The other geometrical parameters are, within limits, temperature independent, and we have no good explanation for this variation in $r(C-C)$. We do not believe the variation to be real.

The geometrical parameters of the CH_2Cl group are as expected when compared with other molecules containing this group [2, 5, 24]. $r(C-Br)$ is slightly longer than in vinylbromide [25], but considerably shorter than in bromoacetylbromide [2] and acetylbromide [26].

The conformational composition showed a uniform and slight increase in the amount of *gauche* conformer as the temperature was increased. The *anti*

TABLE 3

2-Bromo-3-chloro-1-propene: correlation matrix ($\times 100$) for the 20°C refinement; σ_0 are standard deviations from the least squares refinement

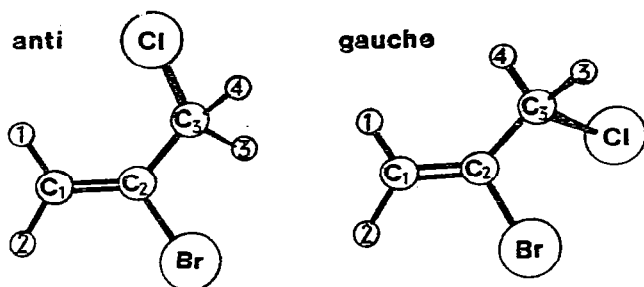| No.	Parameter	σ_0	1	2	3	4	5	6	8	10	15	17
1	$r(C=C)$	0.0035	100									
2	$r(C-C)$	0.0040	26	100								
3	$r(C-Br)$	0.0025	−15	13	100							
4	$r(C-Cl)$	0.0023	14	−15	−27	100						
5	$\langle r(C-H)\rangle$	0.0074	41	18	21	−3	100					
6	$\angle C=C-C_g$	0.32	33	17	25	15	11	100				
8	$\angle C=C-Br_g$	1.00	−6	37	40	−21	24	−50	100			
10	$\angle C-C-Cl_g$	0.86	4	22	41	−26	32	−38	92	100		
15	$\angle\tau_a$	0.86	9	−25	17	−3	−2	−13	−30	−27	100	
17	$\%$ *anti*	3.6	−6	−27	−35	20	−22	19	−57	−54	9	100

Fig. 3. 2-Bromo-3-chloro-1-propene. Atomic numbering for *anti* and *gauche* conformers.

conformer is therefore energetically most stable as was the case for 2,3-di-chloro-1-propene. An ED study of 3-chloro-1-propene gave as the result ca. 80% *gauche* conformer [27] at 20°C. Introducing a vicinal halogen therefore seem to destabilize the *gauche* conformer since BCP in the gas phase contains 52% *gauche* at 20°C. This is also the same result as was found in the liquid phase [6].

The variation in conformational composition with temperature can be used to gain information about the relative energy in the *anti* $\rightleftarrows$ *gauche* equilibrium. The energy difference $\Delta E = E_g - E_a$ and the entropy difference ΔS (excluding the contribution due to the *gauche* form existing as two enantiomeric forms) were calculated from $\alpha_g/\alpha_a = 2(\exp(\Delta S/R))(\exp(-\Delta E/RT))$ where α_g and α_a are the fractions of the two conformers. A Van't Hoff plot of the compositional data (Fig. 4) gave the required information. ΔE and ΔS were assumed to be temperature independent in the actual temperature interval. The best fitted (least squares) line gave $\Delta E = 3 \pm 1$ kJ mol^{-1} and $\Delta S = 4 \pm 3$ J mol^{-1} K^{-1} where error estimates correspond to the standard deviations obtained for α_g and α_a. These values may be compared with the values $\Delta E = 3 \pm 1$ kJ mol^{-1} and $\Delta S = 2 \pm 4$ J mol^{-1} K^{-1} for 2,3-dichloro-1-propene [4], $\Delta E = 3.8 \pm 0.4$ kJ mol^{-1} for 2-chloro-3-fluoro-1-propene
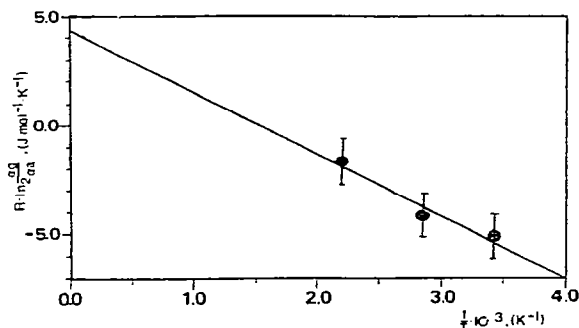

Fig. 4. 2-Bromo-3-chloro-1-propene. Van't Hoff plot of compositional data. The half-lengths of the bars indicate one standard deviation. Least squares straight line.

[28] and $\Delta E = 2.3$ kJ mol^{-1} for bromoacetyl chloride [2]. The conformational composition of all these molecules are similar. However, the error limits are too large to make detailed comparisons possible.

With the assumption that the *anti* torsional motion around the =C—C bond is harmonic, the value of the *anti* torsional force constant, $f_\tau(anti)$, may be approximated from the experimental r.m.s. torsional amplitude as $f_\tau = \frac{1}{2}V^* = RT/\langle(\Delta\tau)^2\rangle$. The result with standard deviation is $f_\tau = 0.12 \pm 0.03$ mdyn Å rad^{-2} and an estimate of $V^* = V_1 + 4V_2 + 9V_3 + \cdots = 150 \pm 30$ kJ mol^{-1}. From the value of f_τ given above, an *anti* torsional frequency of 83 ± 10 cm^{-1} was calculated. There was an observed frequency at 87 cm^{-1} [8] which could not definitely be identified as belonging to only one conformer. The value calculated here combined with the vibrational spectroscopy data indicates that the observation at 87 cm^{-1} may be due to two overlapping bands. However, the uncertainty in $\langle(\Delta\tau)^2\rangle^{1/2}$ is large and caution must be used in making conclusions based on its value.

ACKNOWLEDGEMENTS

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