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Vibrational Spectra, Conformational Composition and Normal Coordinate Analysis of 3-Chloro-1-butene

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The infrared spectra of 3-chloro-1-butene were recorded in the region 4000–50 cm^{-1} for the vapour, liquid, amorphous and annealed solid at 90 K. Raman spectra of the neat liquid, various solutions and amorphous and annealed solid were recorded. Intensity variations observed when going from the liquid to the solid state revealed that two or possibly three conformers were present. The predominant conformer in the vapour and liquid was also present in the crystal. Practically all the fundamentals of this conformer (the one where a hydrogen atom eclipses the double bond) were observed and interpreted. The interpretation was aided by a normal coordinate analysis. At high pressure (above *ca.* 1 kbar), partly isomerization to *trans*-1-chloro-2-butene took place. In an earlier vibrational study of 3-chloro-1-butene several impurity bands of *trans*-1-chloro-2-butene were reported.

Compared to the thorough vibrational study of 3-chloro-1-propene,[1–3] 3-chloro-1-butene (later to be called CB) has received little attention. A few years ago, certain infrared and Raman spectral data were reported.[4] The authors concluded that the two conformers with Cl and CH_3 eclipsing the double bond (II and III, Fig. 1) were nearly equally abundant and coexisted together with a third conformer, having a torsional angle of 180° relative to conformer II.

There is clear experimental evidence that both 3-chloro-1-propene [1–3,5] and 1-butene [6,7] exist predominantly as the conformer in which a hydrogen eclipses the double bond. Thus, the corresponding conformer (I, Fig. 1) is expected to be the most abundant for CB. Preliminary results from a gas phase electron diffraction study of CB [8] reveal that the vapour consists of *ca.* 80 % of conformer I.

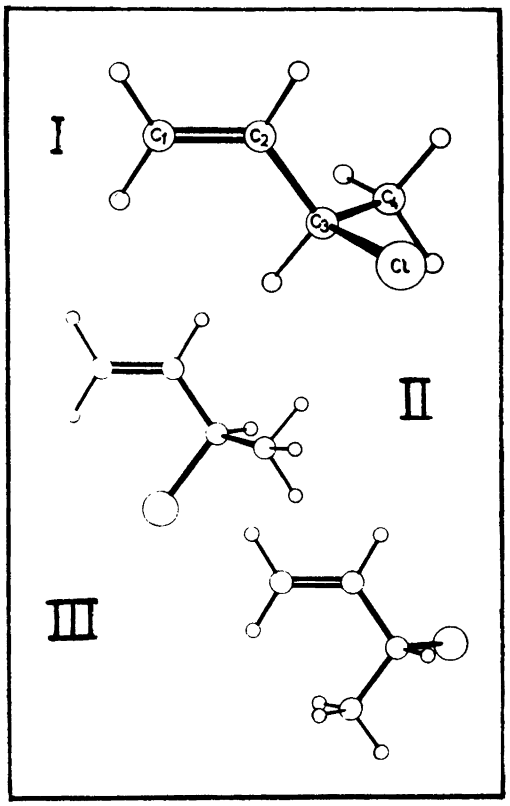

Fig. 1. The probable conformers of 3-chloro-1-butene (CB).

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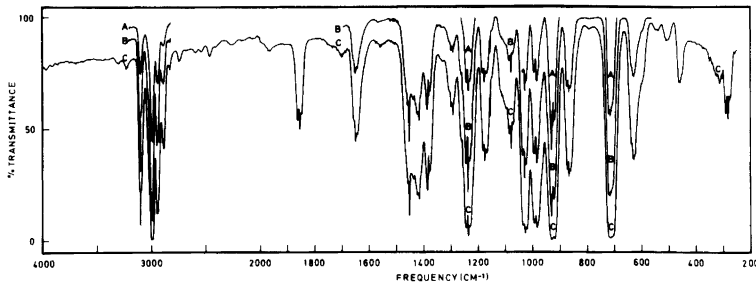

Fig. 2. Infrared spectra of 3-chloro-1-butene as a vapour; path length 10 cm; A, 10 Torr; B, 30 Torr; C, 100 Torr.

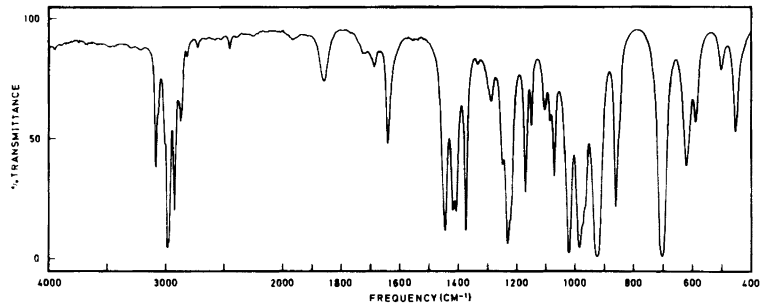

Fig. 3. Infrared spectrum of 3-chloro-1-butene as a liquid, 0.028 mm path length.

The spectra reported earlier [4] show a number of bands as expected when many conformers are present. However, the stronger band corresponding to C=C stretch was found as high as 1670 cm^{-1}, close to the C=C stretching frequency of *trans*-2-butene.[9] This seems surprising, since in propene,[10] 1-butene[11] and 3-chloro-1-propene[1-3] this frequency is close to 1650 cm^{-1}. Thus, it was found worthwhile to reinvestigate and to extend the vibrational study of CB. With three possible conformers coexisting, all of them without symmetry, it was regarded unlikely to discern completely the fundamentals of the less abundant conformers. However, it should be possible to identify the fundamentals of the main form.

EXPERIMENTAL

CB was a commercial product from Aldrich. The sample was purified by preparative gas chromatography, and the spectra were recorded as described previously.[12] The vapour spectra were recorded at 100, 30 and 12 torr in a 10 cm cell with CsI windows and in a 20 cm cell with polyethylene windows. High pressure infrared spectra were recorded in a diamond anvil cell, with spacers of copper and brass. No internal standard was used and the pressures are therefore highly approximative.

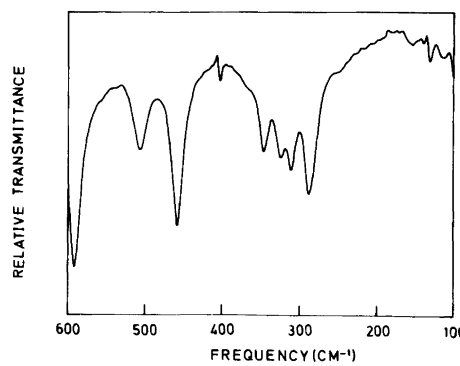

Fig. 4. Far infrared spectrum of 3-chloro-1-butene in benzene solution, path length 1 mm, 3.5 μm beamsplitter.

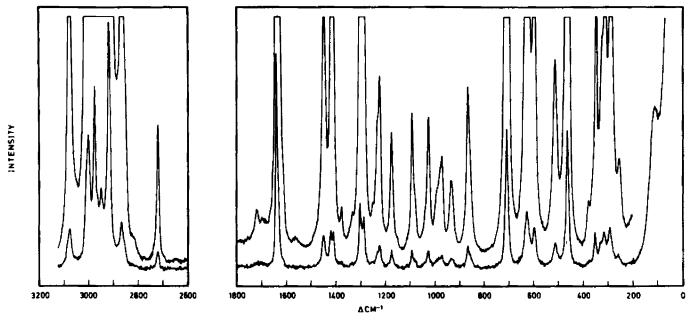

Fig. 5. Raman spectrum of liquid 3-chloro-1-butene.

RESULTS AND DISCUSSION

Infrared spectra of CB in the vapour and liquid states are shown in Figs. 2–4. The Raman spectra of the liquid and amorphous and crystalline solid are given in Figs. 5–6. The observed frequencies are listed in Table 1.

High pressure spectra. Isomerization. Application of high pressure (*ca.* 1 kbar) partly converted CB to *trans*-1-chloro-2-butene. The times before equilibrium composition was obtained were larger the lower the pressure. Within the pressure range used (*ca.* 1–20 kbar), the time varied from *ca.* two hours to practically instant conversion. From gas phase studies the activation energy at atmospheric pressure has been observed [14] to be 197 kJ mol^{-1}.

Approximately equal equilibrium mixtures were measured from a wide range of pressure conditions. The high pressure infrared spectrum (Fig. 7) was compared with liquid state spectra of CB+*trans*-1-chloro-2-butene mixtures. Such a comparison indicates that there is approximately 30 % CB and 70 % *trans*-1-chloro-2-butene in the equilibrium mixture in the high pressure cell. The same ratio was obtained earlier from a study of this equilibrium in toluene solution.[13]

The high pressure apparently reduces further the fairly low barrier (197 kJ mol^{-1}) of isomerization of CB to *trans*-1-chloro-2-butene, without significant changes in the isomeric composition. Therefore, the partial molar volumes $\bar{V}$ of CB and *trans*-1-chloro-2-butene must be almost

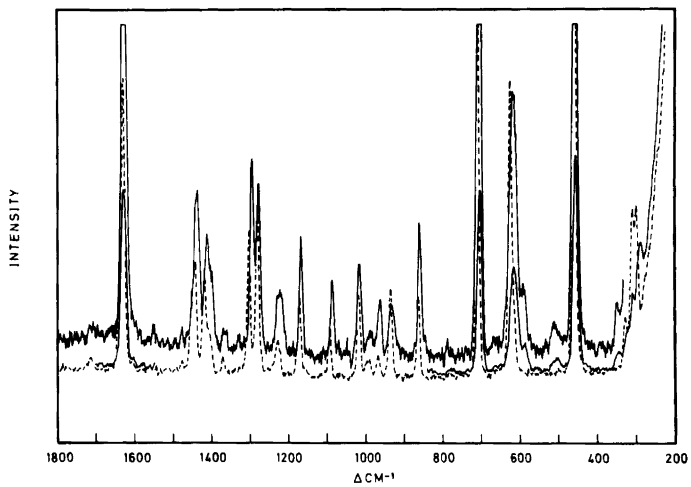

Fig. 6. Raman spectrum of amorphous (—) and crystalline (···) 3-chloro-1-butene at 90 K.

Table 1. 3-Chloro-1-butene, vibrational spectral data.

Infrared				Raman		Interpretation	
Vapour	Liquid	Amorphous (90 K)	Crystalline (90 K)	Liquid	Crystalline (90 K)	I	II/III
3108, 3103, 3098, 3091 s [a]	3090 m	3086 m	3085 m	3091 m	3087 s	ν_1	
3085 sh	3075 sh		*	3070 sh	*		fund.
3026 sh		3032 vvw	*	3025 sh	*		fund.
3001 sh	3014 sh	3012 w	3011 w	3016 s	3015 s	ν_2	
2997, 2994, 2990, 2988 vs	2990 vs	2987 s	2994, 2986 m	2991 vs	2999, 2993 s	ν_3	
2983 s	2978 sh,s	2975 s	2976 s	2979 sh,s	2977 s	ν_4	
2977 sh		2964 sh	2966 sh	2961 m	2965 s	ν_5	
2946, 2943, 2935 s	2931 s	2927 s	2926 s	2930 vs	2929 vs	ν_6	
					2909 w		
2894 m	2895 w		*				fund.
2882 m	2878 w	2877 w	2880 w	2879 m	2881 m	ν_7	
	2868 sh	2861 w	2865 w	2864 sh	2867 w		
2835, 2827 vw	2823 vw	2820 vw					
1860, 1853, 1846 m	1861 w	1874 m	1879 m			$2\times\nu_{21}$	
	1727 vw						
1700 vw	1718 vw	1699 vw	1696 w	1714 vw			
	1689 w	1673 w	1670 w				
1654, 1652, 1649, 1645 m	1644 m	1644, 1636 m	1646, 1634 m	1644 vs	1647, 1640 vs	ν_8	
1641				1635 sh			fund.
1617 sh	1616 sh			1616 sh	1618 vw		
1560 vw				1563 vw	1568 vvw		
1462, 1459 w	1454 sh	1454 sh	*	1450 m	1459 w (*)		fund.
1454, 1452 s	1449 s	1446 s	1448, 1446 s	1445 sh	1449 m	ν_9	
1438, 1430, 1423 s	1423 s	1424 s	1426, 1424 s	1422 m	1425 m	ν_{10}	
1423, 1416, 1411 s	1412 s	1410 s	1402 s	1411 m	1411 w	ν_{11}	
1385, 1380, 1376 s	1378 s	1375 s	1372 s	1380 w	1375 w	ν_{12}	
1338, 1329 vw	1337 vw			1328 vw			

1305 1299	sh	1394 sh	1304 w	1306 w	1304 s	1308 m	ν_{13}	
1294 1291 1287	m	1290 m	1286 w	1283 vw	1288 s	1286 m	ν_{14}	
1260 1258	sh	1253 sh,m	1249 sh	*	1251 vw	*		fund.
1243 1237 1232	vs	1234 vs	1234 s	1230 s	1232 sh,w	1232 w	ν_{15}	
1229 1223 1218	sh	1224 sh		*	1218 w	*		fund.
1183 1177 1169	m	1173 s	1175 s	1177 1175 s	1174 w	1175 w	ν_{16}	
1156 1149	sh	1153 w	1153 w	*	1157 vvw	*		fund.
1116 1112	sh	1107 w	1102 vw	*	1105 vw	*		fund.
1096	sh	1089 w	1092 m	1093 m	1089 w	1096 w	ν_{17}	
1086 1078 1071	m	1075 m	1075 m	1076 vw	1074 sh	*		fund.
1037 1031 1029 1023	vs	1024 vs	1022 vs	1017 vs	1024 w	1020 w	ν_{18}	
996 994	s	989 vs	992 s	994 s	989 sh	996 w	ν_{19}	
984 979	s	979 sh	976 sh	*	978 sh	*		fund.
967	sh	971 sh	967 s	964 s	971 w	968 w	ν_{20}	
935 931 927	vs	928 vvs,br	934 vs	937 vs	930 w	937 m	ν_{21}	
920	s				905 vvw			fund.
868 864 859	s	863 s	862 s	862 s	863 m	866 m	ν_{22}	
856	sh	852 sh		*	843 sh	*		fund.
			710 w	*				fund.
719 714 710 706	vvs	705 vvs	705 vvs	706 vs	708 vs	710 vs	ν_{23}	
636 629 626 622	m	622 m	620 m	620 m	622 s	625 s	ν_{24}	
596	sh	591 w	588 w	*	592 m	*		fund.
512 508 503 498	w	504 w	505 w	*	506 m	*		fund.

462							
456 } m	455 m	454 m	452 m	458 vs	456 vs	ν_{25}	
449							
	402 vw [b]						
	363 vvw		*	370 vw	*		fund.
350 vw	345 w	343 vvw	*	345 m	*		fund.
324 vw	323 w	325 w	325 w	324 sh	326 m	ν_{26}	
311 w	310 w	309 w	309 w	310 m	307 m	ν_{27}	
305 vvw	305 vw	302 vvw	*				fund.
290							
282 } m	286 m	289 w	289 w	289 m	296 m	ν_{28}	
274							
		272 vvw	272 vvw				
254 vw	252 vvw			252 w		ν_{29}	
235 vw							
					128 w		
					117 w		
				105 w		ν_{30}	

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad; *, band vanishing in the crystalline state; fund., fundamental. [b] Liquid infrared observations below 450 cm^{-1} are benzene solution spectra.

equal, or the equilibrium would be displaced towards the isomer with the smallest volume. In the case of conformational equilibria of halocyclohexanes [15] and haloethanes [16,17] the equilibria are quite pressure dependent. The difference in partial molar volumes in these cases were calculated [15–17] from the pressure dependence of the conformational equilibria.

The isomerization of CB explains the large number of bands reported by earlier authors.[4] By comparison with our high pressure spectra, the additional bands were easily assigned to impurities of *trans*-1-chloro-2-butene.

Conformation. As expected, the vapour and liquid phase spectra of CB contain a large number of bands which may be regarded as fundamentals. Since many of these vanish nearly or completely in the crystalline sample, there are obviously at least two conformers present in the vapour and in the liquid. Most bands assigned as a fundamental of the predominant conformer, correspond to a nearby, less intense band of a second conformer. There is no definite evidence of a third conformer. But a third conformer cannot be excluded, since these bands must be of low intensity and may be hidden by bands of the other conformers.

Since all three conformers shown in Fig. 1 have C_1 symmetry, all the Raman lines are polarized and infrared vapour phase contours are *A/B/C*

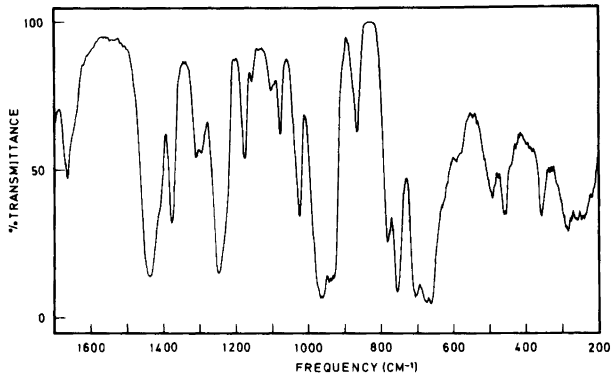

Fig. 7. Infrared spectrum of 3-chloro-1-butene, compressed to *ca.* 20 kbar pressure for *ca.* 4 h.

Table 2. 3-Chloro-1-butene, calculated frequencies for conformers I, II and III (Fig. 1), and corresponding potential energy distribution of I.

Assignment	Frequency				P.E.D.[a]
	I obs.	I calc.[b]	II calc.	III calc.	I
ν_1	3090	3095			$=C_1-H(99)$
ν_2	3014	3022			$=C_2-H(94)$
ν_3	2990	2982			$=C_1-H(95)$
ν_4	2978	2987			$C_4-H(100)$
ν_5	2961[c]	2987			$C_4-H(100)$
ν_6	2931	2931			$C_4-H(100)$
ν_7	2895	2916			$C_3-H(98)$
ν_8	1649	1645	1651	1644	$C=C(82)\ C_2-C_3(15)$
ν_9	1449	1489	1489	1489	$H-C_4-H(93)$
ν_{10}	1423	1488	1488	1488	$H-C_4-H(93)$
ν_{11}	1412	1418	1421	1420	$H-C_1-H(50)\ C=C_1-H(35)$
ν_{12}	1378	1370	1381	1387	$C-C_4-H(49)\ H-C_4-H(44)\ C-C_3-H(12)$
ν_{13}	1304	1362	1369	1369	$C-C_3-H(78)\ C-C_4-H(11)$
ν_{14}	1288	1316	1313	1306	$C=C_2-H(20)\ C_2-C_3(17)\ C-C_4-H(11)$
ν_{15}	1234	1229	1248	1233	$Cl-C-H(45)C-C_3-H(36)C-C_4-H(11)$
ν_{16}	1173	1160	1122	1194	$C_3-C_2-H(29)\ C_2-C_3(25)\ C=C_2-H(18)$
ν_{17}	1089	1078	1081	1007	$C_3-C_4(70)\ C=C_1-H(11)$
ν_{18}	1024	1019	1032	1046	$C-C_4-H(40)\ C=C_1H(19)\ Cl-C-H(11)$
ν_{19}	989	997	1011	1002	$w=CH_2(32)tC=C(31)\ w=CH(24)$
ν_{20}	979	979	984	990	$C-C_4-H(55)\ C=C_1-H(19)\ Cl-C-H(12)$
ν_{21}	928	924	932	931	$w=CH_2(52)\ tC=C(42)$
ν_{22}	863	885	887	872	$C-C_4-H(31)\ C_2-C_3(26)\ C=C_1-H(24)$
ν_{23}	705	747	713	738	$C-Cl(31)\ CC_4H(11)$
ν_{24}	622	618	610	591	$w=CH(38)\ tC=C(18)\ C-Cl(16)$
ν_{25}	455	410	522	501	$C=CC(32)\ C-Cl(21)$
ν_{26}	323	320	341	319	$C-C_3-H(21)\ C-C-C(21)\ Cl-C-C_2(18)\ C=C-C(18)$
ν_{27}	310	294	295	312	$Cl-C-C_4(54)\ Cl-C-C_2(25)$
ν_{28}	286	280	247	284	$C-C-C(38)\ Cl-C-C_2(24)\ Cl-C-C_4(15)$
ν_{29}	252	238	239	300	$tC_3-C_4(96)$
ν_{30}	105[c]	103	85	109	$tC_2-C_3(87)$

[a] Contributions of more than 10 % are included, given as $f_{ij}^2 F_{jj}\lambda_i$. w and t denote out-of-plane wag and torsion, respectively. [b] The force field will appear in Ref. 8. [c] Raman observation, other observed frequencies are infrared liquid data.

hybrids. Solution spectra from various solvents did not show intensity changes which were conformationally significant. It was not possible to decide which informer is predominant from the vibrational spectra alone.

All the bands which appeared in the liquid state spectra and vanished in the spectra of the crystalline sample, had low intensities. This observation strongly indicates that there is one abundant conformer. By comparison with the electron diffraction experiment,[8] this conformer is undoubtedly conformer I (Fig. 1).

Vibrational assignment. Most of the 30 fundamentals of conformer I were interpreted by comparison with the spectra of 3-chloro-1-propene [1-3] and 1-butene.[11] The frequencies associated with the $=CH_2$, $=CH$ and CH_3 groups are close to those of 3-chloro-1-propene and 1-butene. However, there is some uncertainty regarding the description of the C–H stretching modes and the frequencies in the region 1200–950 cm^{-1}.

The complexity of the spectrum in the 1200–950 cm^{-1} region is reflected in the potential

energy distribution of the vibrational modes in this region (Table 2). The calculation was based upon a valence force field, obtained as a combination of corresponding valence force fields for 3-chloro-1-propene and 1-butene (the force field will be published in a forthcoming paper [8]). The calculation shows that the normal modes approximately decribed as $=CH_2$ wag, =CH and C=C twist are highly mixed, as are C=C−H bend, CH_3 rock and C−C stretch. Nevertheless, the description given in Table 2 agrees quite well with those of 3-chloro-1-propene and 1-butene. The spectral interpretation relied heavily upon the results of the force constant calculations.

Normal coordinate calculations were also carried out for conformers II and III, by transferring the force constants from conformer I (Table 2). The calculations indicate that many fundamentals of the most abundant conformer I should overlap or lie very close to those of conformers II and III. 19 cases were observed for which infrared and/or Raman bands present in the liquid or amorphous spectra vanished in the crystal spectra. These bands are assigned as fundamentals of II and/or III, although we cannot exclude that some might be combination bands or overtones of conformers I and II.

Many of the bands which are attributed to conformers II and III agree quite well with the calculated wave numbers. It might have been possible to make systematic assignments of the fundamentals of conformers II and/or III, partly to the vanishing crystal bands and partly to bands of conformer I presumably overlapping those of conformers II and III. Since this procedure would be quite uncertain, it was not attempted.

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