The Vibrational Assignment and Rotational Isomerism of β-Halogenoethyl Mercaptan

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In a previous paper,[1] we dealt with the vibrational spectra of 1, 2-ethanedithiol in relation to the rotational isomerism. The present work, the second of a series of papers, will deal with the vibrational spectra of β-chloroethyl mercaptan and β-bromoethyl mercaptan. We have two objects in studying the spectra of these substances. First, these molecules are suitable for checking the transferability of the force constants obtained from the observed spectra of 1, 2-ethanedithiol. Second, they can be obtained by the exchange of an oxygen in ethylene chlorohydrin with a sulfur atom. For ethylene chlorohydrin, extensive studies were reported by Mizushima and his coworkers[2] about the rotational isomerism. They reported that two rotational isomers exist in the gaseous and the liquid states, where the gauche isomer is more stable than the trans. In the crystalline state, the gauche isomer alone was found to persist. For other 1, 2-disubstituted ethanes, the trans isomer was usually found to be more stable than the gauche, and in

1) M. Hayashi, Y. Shiro. T. Oshima and H. Murata, This Bulletin, 38, 1734 (1965).

2) S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe and M. Yasumi, *J. Chem. Phys.*, **19**, 1477 (1951); S. Mizushima, T. Shimanouchi, K. Kuratani and T. Miyazawa, *J. Am. Chem. Soc.*, **74**, 1378 (1952).

the crystalline state, the trans isomer alone was found to persist. It was understood that this irregularity in the case of ethylene chlorohydrin appears because of the presence of an intramolecular hydrogen bond between a chlorine and a OH group in the gauche form.

Since a SH group is expected to have a very weak power to make a hydrogen bond with a halogen atom, in contrast to the fact that a OH group has a strong power, the findings concerning β-halogenoethyl mercaptan are expected to be interesting.

Experimental

β-Chloroethyl and β-bromoethyl mercaptans were prepared by adding dry hydrochloric acid and hydrobromic acid respectively to ethylene sulfide.

β-Chloroethyl mercaptan: b. p. 113°C/760 mmHg

β-Bromoethyl mercaptan: b. p. 52°C/ 28 mmHg

The purity of the samples was checked by gas chlomatography.

The Raman spectra were measured with a Cary 81 spectrometer, while the infrared spectra were recorded with EPI-S2 (Hitachi Co. Ltd.) with NaCl optics in the region from 4000 to 650 cm^{-1}.

The infrared spectra in the crystalline state were recorded for the samples cooled with liquid nitrogen at about −120°C.

Rotational Isomerism

A comparison of the observed spectra in the gaseous and the liquid states with those in the crystalline state immediately reveals the existence of rotational isomers for these substances, since many infrared bands vanish in the crystalline state.

As we reported in the previous paper, in the case of 1,2-ethanedithiol, large shifts of frequencies may be expected, depending on the molecular forms around the C-C bond, while the molecular forms around the C-S bond will cause rather smaller shifts in frequency. As we have very similar spectra to those of 1,2-ethanedithiol, the above conclusion might also be true for β-halogenoethyl mercaptan. Therefore, we will disregard for a moment the molecular forms around the C-S bond. If the isomers are the trans and the gauche forms around the C-C bond, the trans form might be a less polar form than the gauche form. We may expect then that the spectra for the trans form will get their relative absorption intensities when a mixture is made with a non-polar substance as a solvent, while the spectra for the gauche form will get their relative intensities in a mixture with a polar solvent. Measurements were made with cyclohexane, carbon disulfide, acetone and nitromethane as a solvents for β-chloroethyl mercaptan. Around 750 cm^{-1}, five infrared bands (778, 753, 724, 699 and 675 cm^{-1}) are seen, of which two (675 and 778 cm^{-1}) vanish in the crystalline state. It has been found that the bands at 675 and 778 cm^{-1} become stronger as the solvent becomes polar. Therefore, for β-chloroethyl mercaptan the molecular form in the crystalline state is probably the less polar form or the trans form around the C-C bond, and the other which exists only in the gaseous and liquid states, is probably the more polar form or the gauche form. Similar results have been obtained for β-bromoethyl mercaptan.

The skeletal normal vibration calculation has also given the same conclusion for both substances. We have calculated the skeletal frequencies as a four-body problem in an Urey-Bradley force field with the force constants reported in the literature.[3] They are $K(CH_2\text{-}CH_2)=3.7$, $K(CH_2\text{-}SH)=2.43$, $K(CH_2\text{-}Cl)=2.9$, $K(CH_2\text{-}Br)=2.4$, $H(CH_2\text{-}CH_2\text{-}SH)=0.15$, $H(CH_2\text{-}CH_2\text{-}Cl)=0.17$, $H(CH_2\text{-}CH_2\text{-}Br)=0.15$, $F(CH_2\cdots SH)=0.466$, $F(CH_2\cdots Cl)=0.49$ and $F(CH_2\cdots Br)=0.40$ md./Å. Seven different isomers around the C-C bond were considered as molecular forms.

For these substances there are two skeletal deformation frequencies for an unique molecular form, which would be expected below 500 cm^{-1}. For β-chloroethyl mercaptan, four Raman lines are seen, at 406, 300, 255 and 220 cm^{-1}. It has been concluded from the calculation that 406 and 255 cm^{-1} correspond to the calculated frequencies (406 and 248 cm^{-1}) for the gauche form and that 300 cm^{-1} corresponds to that (282 cm^{-1}) for the trans form. The line at 220 cm^{-1} might not be another skeletal deformation frequency for the trans form even though the calculated frequency is 221 cm^{-1}, since this has been calculated as 186 cm^{-1} from the refined treatment of normal vibrations to be described afterwards, and since the calculation has shown that 220 cm^{-1} might be the C-S torsional frequencies for the gauche form.

For β-bromoethyl mercaptan we have three observed Raman lines, at 210, 245 and 375 cm^{-1}; the calculated frequencies are 375 and 225 cm^{-1} for the gauche form and 235 and 169 cm^{-1} for the trans form. Therefore, 245 cm^{-1} corresponds to that for the trans form, while 210 and 375 cm^{-1} correspond to those for the gauche form. In the gaseous and the liquid states, both the trans and the gauche isomers exist. Measurements of the relative absorption

3) S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953); M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1692 (1956); 78, 627 (1957).

TABLE I. INFRARED AND RAMAN SPECTRA OF β-CHLOROETHYL MERCAPTAN (cm^{-1})

Infrared Gas	Infrared Liquid	Infrared Solid	Raman Liquid	Assignment[a]
			220 vw	torsion
			255 w	skel. def. (G)
			300 s	skel. def. (T)
			406 w	skel. def. (G)
			640 s	C-S str. (G)
675 w	675 sh		680 sh	C-Cl str. (G)
705 sh	702 vs	699 vs	695 s	C-S str. (T)
720 vs	724 m	724 m	720 s	CH_2 rock. (T)
754 vw	754 w	753 s	753 vs	C-Cl str. (T)
766 w	778 m	—		CH_2 rock. (G)
855 w	860 m	860 m	860 m	CSH def. (TT, GT)
—	888 w	—		CSH def. (GG)
920 vw	928 m	—	920 w	CSH def. (TG, GG′)
972 s	969 vs	—	970 w	CH_2 rock. (TG)
1034 m	1021 w	1021 w	1025 m	CH_2 rock. (TT), C-C str. (G)
1052 w	1048 m	1048 s	1045 m	C-C str. (T)
1136 1146 m	1143 s	1143 s	1142 w	CH_2 twist. (T, G)
1226 vs	1227 vs	1224 vs	1210 w	CH_2 wag. (T)
1280 vs	1283 vs	1268 w	1275 sh	CH_2 twist. (T), CH_2 wag. (G)
1296 vs	1298 vs	1294 s	1295 vs	CH_2 wag. (T)
1305 sh	1306 vs	—	1310 sh	CH_2 wag. (G)
1431 vs	1423 s 1445 vs	1421 s 1443 vs	1430 s 1435 s	CH_2 bend. (T, G) CH_2 bend. (T, G)
2570 m	2570 s	2570 s	2570 vs	S-H str. (T, G)
2950 s	2950 vs	2950 vs	2950 vs	C-H str. (T, G)
2995 s	2995 s	2995 s	2990 s	C-H str. (T, G)

a) Molecular forms around the C-C bond are shown in parentheses. For CSH deformations, molecular forms around both the C-C bond and the C-S bond are shown.

intensities of CH_2 wagging frequencies around 1250 cm^{-1} were attempted in order to ascertain the energy differences in the isomers in both the gaseous and the liquid states.

In the gaseous state measurements were made at ten different temperatures in the range from 50 to 160°C. In the liquid state they were made at five different temperatures in the range from −30 to 70°C. The measurements indicated that for these substances the trans isomer is more stable than the gauche isomer in both the gaseous and the liquid state. In the gaseous state the energy differences are computed from the observed optical densities as 0.5_2 and 0.9_5 kcal./mol. for β-chloroethyl and β-bromoethyl mercaptan respectively. In the liquid state they are computed as 0.1_6 and 0.6_2 kcal./mol. respectively.

However, the spectra used for the trans and the gauche isomers are situated so close together that the errors might be expected to be relatively large (±300 cal./mol.).

Normal Coordinate Treatment

The normal vibration calculation has been attempted for two purposes:

1) In order to use the results as an aid in the assignment of the spectra and for the consideration of the detailed molecular forms of the isomers, and

2) In order to test the set of force constants which we obtained from the observed spectra of 1, 2-ethanedithiol and to ascertain whether or not the set is applicable to these substances.

There are five possible molecular forms for these substances. In the notation described in the previous paper, these are TT, TG, GT, GG and GG′ (where the first letter refers to the molecular form around the C-C bond, and the second, to those around the C-S bond). In this treatment all the vibrational freedoms were taken into account, including two torsional freedoms, and a modified Urey-Bradley force field was used which included the following modifications:[4]

(1) Torsional force constants, Y; (2) C-H bond interaction constants, p; (3) angle interaction constants, l, for CH_2 groups, and (4) trans and gauche interaction constants, t and g, between angles of different CH_2 groups.

4) T. Shimanouchi, *Pure and Appl. Chem.*, **7**, 131 (1963); T. Shimanouchi, "Proc. Intern. Sym. Mol. Str. and Spectroscopy," Tokyo, C 216 (1962).

TABLE II. INFRARED AND RAMAN SPECTRA OF β-BROMOETHYL MERCAPTAN (cm^{-1})

Infrared Gas	Infrared Liquid	Infrared Solid	Raman Liquid	Assignment[a]
			210 w	skel. def. (G)
			245 m	skel. def. (T), torsion (T)
			375 w	skel. def. (G)
			555 s	C–Br str. (G)
			612 vs	C–Br str. (T)
665 m	665 w	—	662 m	C–S str. (G)
710 m	710 m	713 s	710 s	CH_2 rock. (T)
743 m	743 m	742 s	735 s	C–S str. (T)
765 m	765 m	—		CH_2 rock. (G)
848 w	852 s	852 s	837 s	CSH def. (TT), (GT)
	858 sh	—		CSH def. (GG)
900 s	903 m	910 m	895 w	CSH def. (TG), (GG′)
950 m	964 vs	—	960 w	CH_2 rock. (TG)
1033 w	1022 w	1022 w	1028 w	CH_2 rock. (TT), C–C str. (G)
	1043 w	1043 m	1045 s	C–C str. (T)
1122 m	1122 vs		1123 w	CH_2 twist. (G)
		1135 vs	1140 s	CH_2 twist. (T)
1199 vs	1199 vs	1199 vs	1195 m	CH_2 wag. (T), CH_2 twist. (G)
1259 s	1260 vs	—		CH_2 wag. (G)
1273 s	1271 sh	1271 vs	1275 vs	CH_2 wag. (T), twist. (T)
1295 sh	1291 s	—		CH_2 wag. (G)
1415 s	1416 s	1419 s	1425 s	CH_2 bend. (T, G)
1431 s	1431 vs	1430 vs	1430 s	CH_2 bend. (T, G)
2570 m	2570 s	2570 s	2562 vs	S–H str. (T, G)
2950 s	2950 vs	2950 vs	2962 sh	C–H str. (T, G)
3000 s	3000 s	3000 s	3010 m	C–H str. (T, G)

a) Molecular forms around the C–C bond are shown in parentheses. For CSH deformations, molecular forms around both the C–C bond and the C–S bond are shown.

There was no modification made between the CSH angle and those of CH_2 groups. Therefore, the force field remained unchanged even when the molecular form around the C–S bond changed. All of five molecular forms were considered for β-chloroethyl mercaptan, while for β-bromoethyl mercaptan only two isomers (TT and GT) were considered. Twenty-six force constants were used in the calculation; among them twenty force constants were transferred from those obtained for 1, 2-ethanedithiol. Six other force constants, which were related to halogen atoms, were determined in order to predict the observed spectra in the best possible way. They are listed in Table III; the calculated frequencies are listed in Tables IV and V with the observed frequencies, which we will discuss afterwards. The agreement between the observed and the calculated frequencies has been found to be very satisfactory; we have concluded that the set of force constants obtained in the previous paper is also applicable to these substances.

Vibrational Assignment and Molecular Form

The assignments of these spectra can easily be found by comparing them with the spectra of 1, 2-ethanedithiol. They are given in Tables I and II. We found differences from the results of 1, 2-ethanedithiol in the region from 950 to 800 cm^{-1}, where we would expect CSH deformation frequencies. In this region, we have four infrared bands for both β-chloroethyl and β-bromoethyl mercaptan. As we have only one CSH deformation frequency for a unique molecular form, these are too many for two isomers.

In the previous paper on 1, 2-ethanedithiol, we noted, from the refined treatment of normal vibration calculations, that C–C stretching, C–S stretching, one of two CH_2 rockings and one of two CSH deformation frequencies are shifted slightly if the molecular form around the C–S bond is different. Since we had no unassigned spectra for 1, 2-ethanedithiol and since the results of normal vibration calculation gave reasonable force constants for the trans form around the C–S bonds, while the gauche form did not, we determined tentatively that the molecular form is the trans around the C–S bond.

The situation is different for β-halogenoethyl mercaptan. For β-chloroethyl mercaptan, the molecular form in the crystalline state is regarded as TT, since, from the absorption

TABLE III. FORCE CONSTANTS

Force constants transferred from the set obtained from 1, 2-ethanedithiol.					
K(C-H)	md./Å	4.33	F(HCS)	md./Å	0.192
K(S-H)	md./Å	3.46	F(HCC)	md./Å	0.459
K(C-C)	md./Å	2.2	F(SCC)	md./Å	0.560
K(C-S)	md./Å	1.9	F(CSH)	md./Å	0.620
H(HCH)	md./Å	0.331	Y(CH_2SH)	md.·Å	0.052
H(HCS)	md./Å	0.294	Y(CH_2CH_2)	md.·Å	0.15
H(HCC)	md./Å	0.156	κ(CH_2S)	md.·Å	0.058
H(SCC)	md./Å	0.052	l(CH_2)	md.·Å	0.057
H(CSH)	md./Å	0.086	t(CH_2CH_2)	md.·Å	0.136
F(HCH)	md./Å	0.2	g(CH_2CH_2)	md.·Å	−0.051
Force constants determined to predict the observed spectra best.					
K(C-Cl)	md./Å	2.0	F(CCCl)	md./Å	0.60
K(C-Br)	md./Å	1.75	F(HCCl)	md./Å	0.20
H(CCCl)	md./Å	0.10	F(CCBr)	md./Å	0.58
H(HCCl)	md./Å	0.29	F(HCBr)	md./Å	0.19
H(CCBr)	md./Å	0.09	κ(CH_2Cl)	md.·Å	0.05
H(HCBr)	md./Å	0.28	κ(CH_2Br)	md.·Å	0.05

$F' = -(1/10)F$ l; interaction term within CH_2 group t, g; trans and gauche interaction terms for CH_2CH_2 group Y; torsional vibration force constant.

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES OF β-CHLOROETHYL MERCAPTAN (cm^{-1})

Trans (C-C)			Gauche (C-C)				
Obs.	Calcd.		Obs.	Calcd.			Assignment
	TT	GT		TG	GG	GG′	
1445	1429	1429	1445	1429	1429	1429	CH_2 bend.
1423	1415	1415	1423	1417	1418	1418	CH_2 bend.
1298	1295	1289	1306	1292	1285	1286	CH_2 wag.
1227	1202	1197	1283	1249	1248	1248	CH_2 wag.
1283	1289	1287		1177	1168	1168	CH_2 twist.
1143	1157	1159	1143	1145	1146	1145	CH_2 twist.
1121*	1015	985	969	971	968	966	CH_2 rock.
724	709	705	778	774	775	760	CH_2 rock.
1048	1024	1028	1021	1010	1000	986	C-C str.
754	724	713	675	657	652	657	C-Cl str.
702	688	689	640	625	628	626	C-S str.
860*	857	907	860*	850	889	919	CSH def.
300	303	304	406	418	424	417	skel. def.
	186	186	255	258	260	277	skel. def.
(220)	246	253	(220)	221	221	208	torsion
	119	118		102	100	101	torsion

* The values are the observed frequencies for trans form around C-S bond. Observed frequencies for other forms should be referred to Table I.

intensity measurements in mixtures, the bands persisting in the crystalline state are found to be the less polar form and since one of two CH_2 rocking modes in the higher frequency was calculated to be 1015 cm^{-1} for TT, and 985 cm^{-1} for TG, while we have only 1021 cm^{-1} in the crystalline state and no corresponding band can be seen around 985 cm^{-1}. In the region from 950 to 800 cm^{-1}, there is only one infrared band, at 860 cm^{-1}, in the crystalline state. Therefore, this is assigned to the CSH deformation mode for the TT isomer. We have two other bands in this region where no other vibrational modes is to be expected, except for CSH deformation modes. Therefore, we may conclude that more polar form is not a unique molecular form but a group of isomers.

From the normal vibration calculation described in the preceding section, we have

TABLE V. OBSERVED AND CALCULATED FREQUENCIES OF β-BROMOETHYL MERCAPTAN (cm^{-1})

Trans (TT)		Gauche (TG)		Assignment
Obs.	Calcd.	Obs.	Calcd.	
1431	1428	1431	1428	CH_2 bend.
1416	1418	1416	1417	CH_2 bend.
1271	1294	1291	1291	CH_2 wag.
1199	1201	1260	1245	CH_2 wag.
1271	1275	1199	1172	CH_2 twist.
1135	1150	1122	1141	CH_2 twist.
1022	1013	964	968	CH_2 rock.
710	708	765	774	CH_2 rock.
1043	1022	1022	1007	C-C str.
743	715	665	667	C-S str.
612	623	555	557	C-Br str.
852	856	852	849	CSH def.
245	251	375	392	skel. def.
	173	210	215	skel. def.
(245)	246	(245)	255	torsion
	112		86	torsion

also relatively large shifts in frequency for the CSH deformation, and one of two rocking modes for β-chloroethyl mercaptan, for different isomers around the C–S bond. For CH_2 rocking modes we have so many spectra in the expected region that the overlapping of the spectra might hide the differences. However, for CSH deformation modes we have found infrared bands corresponding to the calculated frequencies for different isomers. That is, 928 cm^{-1} corresponds to the calculated frequency, 907 cm^{-1}, for TG and to that, 919 cm^{-1}, for GG', 888 cm^{-1}, to the calculated frequency, 989 cm^{-1}, for GG, and 860 cm^{-1}, to the calculated frequency, 857 cm^{-1}, for TT and to that, 850 cm^{-1}, for GT. We could not determine whether all five isomers exist or not. However, at least three rotational isomers definitely exist, TT, GG and either TG or GG'. For β-bromoethyl mercaptan, we have also found results similar to those in the case of β-chloroethyl mercaptan, since we have similar spectra for CSH deformation modes. This substance, though the band at 903 cm^{-1} is assigned to either TG or GG', might have a component arising from impurity; it persists in the crystalline state, the absorption intensity rapidly increases as the temperature increases in the gaseous state, and the band never loses its intensity again, even when it was cooled to room temperature.

For GG', there is a possibility of finding an intramolecular hydrogen bond between a SH group and a halogen atom. However, we could not find any evidence, though careful measurements were made with different solvents for SH stretching modes around 2570 cm^{-1}.

It should be noted that, even when the trans isomer consists of two molecular forms (TT and TG) and the gauche isomer consists of three molecular forms (GG, GT and GG'), the influences can not be seen for frequencies other than for CSH deformation frequencies; that is, the spectra for all the components coincide with each other except for CSH deformation modes. Therefore, we can find only two sets of the spectra for the trans and the gauche forms around the C–C bond. The assignments are shown in Tables I and II.

Comparison with Ethylene Chlorohydrine

The following are the differences between the results for β-halogenoethyl mercaptan and those for ethylene chlorohydrin:

	β-Halogenoethyl mercaptan	Ethylene chlorohydrin
1) Molecular form around the C–C bond in the crystalline state	trans	gauche
2) More stable molecular form around the C–C bond in the gaseous state	trans	gauche
3) More stable molecular form around the C–C bond in the liquid state	trans	gauche
4) Intramolecular hydrogen bond between XH and a halogen (X=O and S)	not be found	exists
5) Molecular form around the C–S bond	several isomers	not proved

It is very clear from the above comparison that the irregularity of the molecular form in the crystalline state and the stabilities in the gaseous and the liquid states for ethylene chlorohydrin come from the influences of the intramolecular hydrogen bonding between OH and Cl, as Mizushima and his co-workers pointed out. The results for β-halogenoethyl mercaptan strongly confirm this conclusion. For β-halogenoethyl mercaptan, the lack of the intramolecular hydrogen bonding probably makes it easy to find the different isomers around the C–S bond, since this makes the CSH deformation bands of these substances sharper than the COH deformation bands of ethylene chlorohydrin.

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