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Rotational Isomerism and Vibrational Assignments of Monobromothioacetic Acid

H. S. RANDHAWA* and W. WALTER

Institut für Organische Chemie und Biochemie der Universität Hamburg, Federal Republic of Germany

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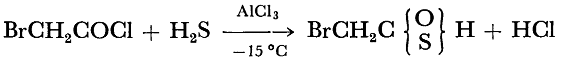
Synopsis. The infrared and Raman spectra of monobromothioacetic acid have been recorded and vibrational assignments proposed for the two symmetrical rotational isomers present in the acid.

In our earlier paper[1] we have investigated the vibrational and NMR spectra of mono- and dichlorothioacetic acids in relation to the rotational isomerism and hydrogen bonding. As a part of the aforesaid studies we had the occasion to synthesize mono- and dibromothioacetic acids. In the present article we have characterized monobromothioacetic acid and made vibrational assignments corresponding to the two symmetrical rotational isomers present in this acid.

Experimental

Monobromothioacetic acid was prepared by the following reaction:



$$BrCH_2COCl + H_2S \xrightarrow[-15\,^{\circ}C]{AlCl_3} BrCH_2C\left\{\begin{matrix}O\\S\end{matrix}\right\}H + HCl$$

The diethyl ether extract of the reaction mixture was distilled thrice under vacuum. The deep yellow colored liquid with bp 27—28 °C/0.2 mmHg; $n_D^{20}=1.5643$ collected under dry nitrogen was used in the spectral measurements and for characterization. The yield was 35%. Elemental analysis: $BrCH_2C\left\{\begin{matrix}O\\S\end{matrix}\right\}H$(27—28 °C/0.2 mmHg): Found: C, 15.35; H, 2.11; Br, 51.73; S, 20.43%. Calcd: C, 15.48; H, 1.93; Br, 51.61; S, 20.64%.

The spectra were recorded by the same apparatus as described in a previous paper.[1] The infrared and Raman band frequencies (in cm^{-1}) along with the relative intensities are given in Table 1. The NMR signals (in 3% $CDCl_3$/TMS) for SH and CH_2 protons were found to be at δ values of 4.8 and 4.00 ppm respectively.

Results and Discussion

Table 1 reveals that the number of normal motions observed in the Raman (liquid) and infrared (liquid film and vapors) spectra are more than the expected number of vibrations *i.e.* $3N-6=12A'+6A''$. In transition from liquid to gaseous phase, a change in relative intensity of some of the infrared bands (Table 1) is observed. Moreover three and two bands were observed in the C–Br and C–S stretching regions respectively, while two bands were observed for each of the C=O stretching and CSH in-plane deformation regions. All these experimental observations show that there are two symmetrical rotational isomers present in the liquid and gaseous states of this acid like its chloro analogue *i. e.* $ClCH_2CO\left\{\begin{matrix}O\\S\end{matrix}\right\}H$.[1]

TABLE 1. INFRARED AND RAMAN BAND FREQUENCIES (in cm^{-1}) OF MONOBROMOTHIOACETIC ACID

Raman Liquid	Infrared		Assignment, species
	Liquid film	Vapor	
3010 m, dp	3000 m	—	CH_2 asymstr, A″
2948 vst	2943 m	2955 w, 2920 w	CH_2 symstr, A′
2560 vst	2544 vst	2582 vw	SH str, A′
1699 m, 1685 m	1715 vst, 1680 vst	1720 vst, —	C=O str, A′
1415 w, 1390 mw	1410 st, 1385 vst	1410 w, —	CH_2 scissor, A′
1250 m, 1215 mw	1245 sh, 1210 st	—, 1210 w	CH_2 wag, A′
1160 vw, 1140 vw	1150 st, —	1155 sh, 1125 st	CH_2 twist, A″
1050 vw, 1090 vw	1035 vst, 1087 sh	1025 st, 1070 mw	C-C str, A′
910 w, 865 m	905 m, 840 m	900 m, 840 m	CSH bend, A′
750 st, 725 m, 710 m	735 m, 705 w	—	C-Br str, A′
655 m, 565 m	—	—	C-S str, A′
450 m, 525 st	—	—	OCS bend, A′
430 m	—	—	CSH bend, A″
410 vw, 398 vw, dp	—	—	C=O wag, A″
255 m, 330 m	—	—	CCBr bend, A′
180 mw, 153 mw, dp	—	—	C-C torsion, A″

dp, depolarized; st, strong; vst, very strong; m, medium; mw, medium weak; sh, shoulder; w, weak; vw, very weak; sym, symmetric; asym, asymmetric; str, stretch; the rotational isomers are assumed to be symmetrical.

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* To whom all queries should be made: H. S. Randhawa, Department of Chemistry, Punjab Agricultural University, Ludhiana, India.

There is strong resemblance between the spectra of thioacids and their corresponding acyl halides.[1] Thus from the well known spectra of $BrCH_2COCl$[2] and $ClCH_2C\begin{Bmatrix}O\\S\end{Bmatrix}H$[1] the assignments of the vibrational motions for the $BrCH_2$–C– and COSH structural parts of $BrCH_2C\begin{Bmatrix}O\\S\end{Bmatrix}H$ are made and given in Table 1. The difference between the IR and Raman band frequencies (Table 1) *e. g.* for SH and C=O stretching modes may be due to the cyclic H-bonded dimers as in the carboxylic acids. The position of SH stretching motion at higher wave number in the vapor phase than in the liquid phase infrared spectrum is the normal behavior of an SH group.[3,4]

Our assignments for the normal motions of this acid are in good agreement (except for the C–C torsional frequency) with those of Nakagawa *et al.* on $BrCH_2$-COCl.[2] The bands positioned at 181 cm^{-1} and 157 cm^{-1} in $BrCH_2COCl$[2] have been assigned to the inplane bending vibration. Since the C–C torsional frequency must be influenced by the mass of the halogenated and thiocarboxyl groups, we prefer to assign the depolarized Raman bands at 180 and 153 cm^{-1} in $BrCH_2C\begin{Bmatrix}O\\S\end{Bmatrix}H$ to the A″ C–C torsional vibration for each of the two rotational isomers. These bands are positioned at 205 and 180 cm^{-1} in $ClCH_2C\begin{Bmatrix}O\\S\end{Bmatrix}H$.[1]

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References

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