Journal of Molecular Structure, 38 (1977) 89—95

VIBRATIONAL AND NMR SPECTRA OF MONO- AND DI-CHLOROTHIOLACETIC ACIDS IN RELATION TO ROTATIONAL ISOMERISM AND HYDROGEN BONDING

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(First received 23 July 1976; in revised form 25 October 1976)

ABSTRACT

The vibrational spectra of mono- and di-chlorothiolacetic acids have been measured in liquid and gaseous states and solutions, and vibrational assignments have been proposed. The experimental material shows that these molecules are present as a mixture of two rotational isomers. The energy of the two isomers in the liquid state is almost the same.

INTRODUCTION

Spectroscopic evidence on the rotational isomerism in mono- and di-halogenated acylhalides is reported in the literature [1, 2]. The resemblance between the vibrational spectra of acylhalides and their corresponding thiolacids is striking [3, 4]. Very recently, infrared studies on thiolpropionic acid in relation to hydrogen bonding and rotational isomerism have been reported by Crowder [4]. To the best of our knowledge no such investigations have been made so far on mono- and di-halogenated thiol acids. Therefore, the present article is devoted to the vibrational spectra of mono- and di-chlorothiolacetic acids in relation to rotational isomerism. The low temperature NMR spectra have also been investigated in order to observe hydrogen bonding and rotational isomerism in these acids.

EXPERIMENTAL

The mono- and di-chlorothiolacetic acids were prepared by the following reaction [5]

$$RCOCl + H_2S \xrightarrow[-15\,^{\circ}C]{AlCl_3} RCOSH + HCl;\ R = CH_2Cl \text{ and } CHCl_2$$

The respective reaction mixtures were distilled twice and the acids with

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B.P. 46°C/16 mm and 56°C/16 mm respectively were used in the present spectral measurements.
Elemental analysis:

$CH_2ClCOSH$ (46°C/16 mm): Found: C 21.74; H 2.76; S 29.10; Cl 31.97.
Expected: C 21.71; H 2.71; S 28.95; Cl 32.11.
$CHCl_2COSH$ (56°C/16 mm): Found: C 16.84; H 1.42; S 21.92; Cl 48.71.
Expected: C 16.55; H 1.31; S 22.06; Cl 49.05.

The deuterated mono-chlorothiolacetic acid was prepared by the direct exchange of acid with heavy water. Deuteration was of the order of 80%.

$$2\,CH_2ClCOSH + D_2O \rightarrow 2\,CH_2ClCOSD + H_2O$$

The infrared spectra of a thin film and vapors of these acids were recorded in the region 4000—540 cm^{-1} using NaCl windows and a gas cell fitted with NaCl windows respectively on a Perkin-Elmer Grade 421 Spectrophotometer. The wavenumbers (cm^{-1}) for mono- and di-chlorothiolacetic acids are presented in Tables 1 and 2 respectively.

The Raman spectra of neat acids and their solutions in benzene and methyl cyanide were recorded on a Cary 82 spectrophotometer, using the 6471 Å line of a Kr laser. The Raman band frequencies (in cm^{-1}) for these acids are reported in Tables 1 and 2.

The room and low temperature NMR measurements were made on a Varian NV-14 spectrometer.

RESULTS AND DISCUSSION

Since the molecules $ClCH_2COSH$ and $Cl_2CHCOSH$ belong to the C_s point group symmetry, all the normal modes should be infrared and Raman active. The total number of motions for one configuration is $3N—6 = 12a' + 6a''$. However the number of Raman lines in the liquid state spectra of these acids is larger than this figure as can be seen from Tables 1 and 2. We have observed two infrared and two Raman lines corresponding to the carbonyl group in both acids (Tables 1 and 2). The number of infrared and Raman band frequencies (Tables 1 and 2) in the 560—800 cm^{-1} region (expected for the C—Cl and C—S stretching vibrations) is also more than the expected number. In transition from liquid to gas phase, a change in relative intensity of some of the infrared bands over the range 560—1100 cm^{-1} is observed (Tables 1 and 2).

The intensity of one set of bands increases in the polar solvent in CH_3CN while that of the other increases in the non polar solvent i.e. C_6H_6. On the basis of the relative change in intensity with the polarity of the solvents, the frequencies have been grouped together as (710, 590); ($\substack{760\\770}$, 800) for $ClCH_2COSH$ and (237, 180); (265, 265); (330, 405); (458, 535), (565, 640) for $Cl_2CHCOSH$. The pairing of vibrational modes is in close agreement with the corresponding acylhalides [1, 2]. The first number of each pair

TABLE 1

Infrared and Raman band frequencies (in cm^{-1}) of mono-chlorothiolacetic acid

Raman (liquid)		Infrared		Assignment	Species
d_0	d_1	(Film)	(Vapor)		
—	—	—	3580 vw	OH str*	A'
—	—	3410 w	3420 w, 3380 w	2×1715: 2×1685	—
—	—	3345 w	—	OH H-bonded*	—
3000 m	3000 m	2995 m	—	CH_2 asym str	A''
2940 vst	2940 vst	2940 m	2950 w	CH_2 sym str	A'
2565 vst	1865 st	2555 st	2585 vw	SH str	A'
—	—	1900 bw	—	—	—
1699 m, 1678 m	1699 m, 1680 m	1715 vst, 1685 vst	1715 vst, 1702 vst	C=O str	A'
1400 m	1400 m	1400 st	1410 w	CH_2 scissor	A'
1290 w, 1260 w	1288 w, 1260 vw	1282 m, 1255 m	—, 1250 w	CH_2 bend	A'
1170 w, 1145 vw	1170 w, —	1170 m, —	—, 1150 vw	CH_2 twist	A''
1135 vw	—	—	—	—	—
1110 vw	—	—	—	—	—
—, 1050 w	—	1085 st, 1045 st	1087 m, —	C—C str	A'
1030 w	1025 w	1030 st	1025 w	—	—
865 m, 900vw	645 w, 685 w	870 m, —	875 w, —	CSH bend	A'
790 m, $\begin{cases}770\text{ st}\\760\text{ st}\end{cases}$	782 m, $\begin{cases}770\text{ w}\\760\text{ st}\end{cases}$	785 st, —	780 m, —	C—Cl str	A'
590 st	590 st	710 st	710 st	C—S str	A'
515 vw, 500 vw	—	—	—	CH_2Cl rock	A'
450 st	—	—	—	CSH bend	A''
438 st	438 st	—	—	OCS bend	A'
400 vw	—	—	—	C=O wag	A''
298 m, 375 m	—	—	—	CCCl bend	A'
288 m	—	—	—	CCS bend	A'
205 w, 180 w	205 w, 180 w	—	—	C—C torsion, dp	A''

Abbreviations used have the following meanings. sym, symmetric; asym, asymmetric; str, stretch; w, weak; mw, medium weak; st, strong; vw, very weak; vst, very strong; bw, broad weak; OH* stretch could be due to the traces of thion tautomer in the acid. The rotational isomers are assumed to be symmetrical.

corresponds to the more polar form and the latter to the less polar form. The total number of experimental facts is explained by the assumption that these acids exist as mixtures of rotational isomers just like their respective acyl halides.

Since the mass of the SH group is very close to that of the Cl atom, the observed vibrational frequencies of $ClCH_2COSH$ and $Cl_2CHCOSH$ will not differ from $ClCH_2COCl$ and $Cl_2CHCOCl$. The behaviour of vibrational motions in different phases has also been found to be similar in thiolacids and their corresponding acyl halides [4].

Thus from the well known spectra of mono- and di-chloroacetylchlorides [1, 2], the assignments of the vibrational motions for the $ClCH_2$—C— and Cl_2CH—C— structural parts of the aforesaid acids can easily be made. The wavenumbers along with assignments of the aforementioned structural parts are presented in Tables 1 and 2.

Concerning the vibrations of the —COSH group, there is no doubt that two Raman lines and two infrared lines observed around 1700 cm^{-1} (Tables 1 and 2) for each of the two acids can be assigned to the C=O stretching vibrations of the two rotational isomers.

TABLE 2

Infrared and Raman band frequencies (in cm^{-1}) of di-chlorothiolacetic acid

Raman	Infrared		Assignment	Species
(Liquid)	(Film)	(Vapor)		
—	—	3575 vw	CH str (Free)	A'
—	3440 m	3460 w, 3420 w	2 x 1715 2 x 1690	—
—	3370 m	—	H—bonded OH	—
3000 st	2998 st	2998 m	CH str	A'
—	2780 vw	—	—	—
—	2740 vw	—	—	—
2579 st	2558 st	2590 vw	SH str	A'
—	2380 vw	—	—	—
—	2340 vw	—	—	—
—	1880 vw	—	—	—
1705 m, 1695 m	1715 vst, 1690 vst	1720 vst, —	C=O str	A'
—	1570 m	1565 vw	—	—
—	1365 m	1355 vw	—	—
1275 bw, 1230 w	1275 sh, 1220 st	1270 vw, 1218 st	CH bend	A'
1210 w, 1215 w	1200 st, —	—	CH bend	A''
1100 w, 1050 w	1098 st, 1045 st	1100 st, 1045 m	C—C str	A'
1030 w	1030 st	1025 st	—	—
890 mw, 910 w	890 st, —	888 m, —	CSH bend	A'
800 mw, 770 w	800 st, 770 st	—, 780 st	CCl_2 asym str	A''
750 m, 725 mw	745 st, 720 st	750 st, —	CCl_2 sym str	A'
565 m, 640 vw	625 m	—	C—S str	A'
458 m, 535 m	—	—	OCS bend	A'
465 m, 498 w	—	—	CSH bend	A''
515 w	—	—	C=O wag	A''
425 vw	—	—	CCS bend	A'
330 m, 405 m	—	—	CCl_2 bend	A', A''
310 w	—	—	$CHCl_2$ rock	A'
265 m, 265 m	—	—	$CHCl_2$ rock	A''
180 m, 237 mw	—	—	C—C torsion dp	A''

The abbreviations have their usual meanings. The rotational isomers are assumed to be symmetrical.

The C—S stretching frequency is generally observed as a strong band in the Raman spectra of thiolacids [6, 1, 7]. In our spectra we find bands at 590 cm^{-1} (Raman) and 710 cm^{-1} (infrared) in $ClCH_2COSH$ (Table 1) and at 565 cm^{-1} (Raman) and 640 cm^{-1} (Raman) in $Cl_2CHCOSH$ (Table 2). These can be assigned to the C—S stretching vibrations of the two rotational isomers in the above mentioned acids. These wavenumbers compare with $ClCH_2COCl$ and $Cl_2CHCOCl$ values at obs. (575 cm^{-1}, 715 cm^{-1}); calc. (600 cm^{-1}, 715 cm^{-1}) and obs. (580 cm^{-1}; 631 cm^{-1}); calc. (595 cm^{-1}, 727 cm^{-1}) respectively.

The SH stretching vibration is seen as a single band around 2550 cm^{-1} in liquid and 2600 cm^{-1} in vapor phase in both the acids (Tables 1 and 2). The wave number in the vapor phase is about 30 cm^{-1} higher than in the liquid phase, which is normal for the SH group [6, 7]. The SH stretching vibration of $ClCH_2COSH$ is lowered on deuteration to 1865 cm^{-1} (Table 1) and is in close agreement with that observed in other thiolacids [7]. The difference between the IR and Raman frequencies (Tables 1 and 2) e.g. for SH and C=O stretching modes may be due to cyclic H-bonded dimers as in the carboxylic acids.

The expected region for the CSH in-plane and CSH out-of-plane bending motions is around 850 cm^{-1} and 450 cm^{-1} respectively [7]. Hence use is made of the spectra of $ClCH_2COSD$ (Table 1) as an aid in the assignment of the CSH bending vibrations. In the deuterated species we would expect the CSH deformation modes to be shifted strongly to the lower frequency region, when no other motions except SH stretching vibration are expected. Actually we observed that two new bands are present at 645 and 685 cm^{-1} in the Raman spectra of $ClCH_2COSD$ (Table 1). A simple application of the product rules reveals that the 865 cm^{-1} and 900 cm^{-1} bands should be the CSH deformation vibrations corresponding to the CSD deformation vibrations at 645 and 685 cm^{-1}. Thus the bands at 890 and 910 cm^{-1} in $Cl_2CHCOSH$ (Table 2) can safely be assigned to the CSH in plane bending vibrations for each of the two rotational isomers.

The band at 450 cm^{-1} in $ClCH_2COSH$ which disappears on deuteration could be due to the CSH out-of-plane deformation. Its counterpart in $CHCl_2COSH$ lies at 465 cm^{-1} (Table 2).

The expected region for the OCS bending vibration in thiolcarboxylic acids is in the range 430—500 cm^{-1} [1, 6—9]. Since the mass of the SH group is very close to that of the Cl atom and also mono- and di-chlorothiolacetic acids show rotational isomerism like their respective mono- and di-chloroacetyl chlorides, one would expect two bands for OCS deformation (one for each isomer) in both acids. In mono- and di-chloroacetylchlorides [1, 2], the bands positioned at (448 cm^{-1}, 559 cm^{-1}) and (461 cm^{-1}, 503 cm^{-1}) respectively are assigned to the OCCl bending motion. Their counterparts in our Raman spectra of $ClCH_2COSH$ (Table 1) and $Cl_2CHCOSH$ (Table 2) are centred at (438 cm^{-1}, —) and (458 cm^{-1}, 535 cm^{-1}) respectively.

In our assignments we disagree with the assignment of the bands at (214 cm^{-1}, 187 cm^{-1}) in $ClCH_2COCl$ and (237 cm^{-1}, 176 cm^{-1}) in $Cl_2CHCOCl$ to the in-plane bending vibrations [1, 2]. In our Raman spectra we find two bands in this region for each of the two rotational isomers in both acids. These bands are centred at (205 cm^{-1}, 180 cm^{-1}) in $ClCH_2COSH$ and (180 cm^{-1}, 237 cm^{-1}) in $Cl_2CHCOSH$ and are depolarized. Therefore we prefer to assign these bands to the A'', C—C torsional vibration.

A comparison of some of the important vibrational modes of the —COSH group of some thiol acids is presented in Table 3.

TABLE 3

A comparison of some of the important vibrational frequencies (in cm^{-1}) of thiol acids

Vibrational mode	SH str	C=O str	C—S str	C—C str	CSH(I/P) def	OCS def
Acids						
HCOSH[a]	2540	1661	690	—	727	494
CH_3COSH[b]	2550	1696	626	993	832	432
C_2H_5COSH[c]	2567	1721[g]	598, 712	—	845	—
CCl_3COSH[d]	2575	1715	500	1060	908	478
CF_3COSH[e]	2578	1739, 1717	747	1289	865	509
$ClCH_2COSH$[f]	2555	1715, 1685	590, 710	1045, 1085	865, 900	438, —
$Cl_2CHCOSH$[f]	2558	1715, 1690	565, 640	1050, 1098	890, 910	458, 535

[a]Ref. (8); [b]ref. (7); [c]ref. (4); [d]ref. (6); [e]ref. (9); [f]present studies; str, stretch; def, deformation; [g]in CCl_4.

The infrared intensity of the C—C stretching modes in both acids was measured at room temperature, and at the temperatures of ice—water, ice—alcohol, and ice—salt mixtures. It was found to remain the same at these temperatures showing that the isomers in both acids have almost the same energy in the liquid state.

NMR STUDIES

The NMR spectra of $ClCH_2COSH$ and $Cl_2CHCOSH$ were measured in $CDCl_3$ using TMS as a reference. In $ClCH_2COSH$, the signal for the CH_2 and SH protons are observed at 4.10 ppm and 4.63 ppm respectively while in $Cl_2CHCOSH$ their counterparts are seen at 5.86 ppm and 4.83 ppm respectively. The low temperature NMR spectra of these acids in the temperature range −15 to −114°C using ($CDCl_3$ + CS_2) as solvent and TMS as reference have also been recorded. The positions of the SH protons in $ClCH_2$ COSH and $Cl_2CHCOSH$ are at 5.05 ppm and 5.08 ppm respectively while those of the CH protons are at 4.26 ppm and 6.03 ppm respectively. The half band width of the SH proton in the aforesaid temperature range varies from 0.8 to 3.2 Hz in $ClCH_2COSH$ and from 1.0 to 6 Hz in $Cl_2CHCOSH$. This change may be due to the presence of intermolecular hydrogen bonding through the SH bond.

The order of association as predicted from the half band width follows the order

$Cl_2CHCOSH > ClCH_2COSH$

The NMR spectra fail to provide any evidence for the existence of rotational isomerism in these acids.

ACKNOWLEDGEMENTS

One of the authors, Dr. H. S. Randhawa, is grateful to the Alexander von Humboldt Stiftung for financial assistance. Thanks are also due to Claus O. Meese for NMR measurements. Dr. H. S. Randhawa is also grateful to Mr. Didschun and Mrs. Schlichting for helping him in all walks of life during his stay in Germany. The authors wish to express their appreciation to Prof. W. J. Orville-Thomas of Salford University for valuable suggestions.

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