BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3480—3482 (1972)

## Molecular Vibrations and Force Fields of Alkyl Sulfides. V. Infrared Spectra of Methyl Isopropyl Sulfide

Masaru Ohsaku, Yuji Shiro,\* and Hiromu Murata

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima \*Shinonome Branch School, Faculty of Education, Hiroshima University, Shinonome-3-chome, Hiroshima (Received May 4, 1972)

A vibrational treatment of methyl isopropyl sulfide was made by McCullough et al.,1) who suggested the existence of two rotational isomers,  $C_1$  (G) and  $C_8$  (T), on the basis of their vibrational data; they claimed that the  $C_1$  form is stable in the solid state. Lately, Scott and El-Sabban<sup>2)</sup> carried out a normal coordinate treatment of this sulfide using a valence force field, and concluded that only the  $C_1$  conformation exists, while the  $C_s$  conformation must have too high energy to exist even in the liquid state. In this paper, in order to overcome the above-mentioned disagreement among the conformational analyses of methyl isopropyl sulfide, and in order to obtain complete infrared data, we newly recorded the infrared spectra in the gaseous, liquid, and solid states; we have then tentatively assigned the observed bands.

## Results and Discussion

The obtained infrared data of methyl isopropyl sulfide are summarized in Table 1. In the C-H

stretching, the CH3 degenerate deformation, and the CH<sub>3</sub> symmetrical deformation, the spectra obtained are well-resolved. In the 1500—1400 cm<sup>-1</sup> region the CH<sub>3</sub> degenerate deformation, in the 1400—1300 cm<sup>-1</sup> region, the CH3 symmetrical deformation, and in the 1300—800 cm<sup>-1</sup> region, the C-H in-plane and out-ofplane bending, CH<sub>3</sub> rocking, and C-C stretching bands are expected. In the last region, there are some bands which disappear in the crystalline state. Most of the bands which disappear in the crystalline state may be due to the less stable conformation. Here, the existence of the rotational isomers can be suggested for this sulfide. The existence of the rotational isomers, however, is more clearly shown in the C-S stretching and skeletal deformation regions. Methyl isopropyl sulfide has two C-S stretching vibrational freedoms for one comformation. In the liquid state, four bands appear; two bands remain in the solid state. In the skeletal deformation region, 500-200 cm<sup>-1</sup>, about five bands, including two torsional bands, are expected for one conformation. In this region, eleven bands appear

Table 1. Infrared frequencies  $(cm^{-1})$  and assignments of methyl isopropyl sulfide<sup>8)</sup>

Gaseous Room Temp.	Liquid Room Temp.	CS <sub>2</sub> soln. Room Temp.	Solid		Assignment <sup>b)</sup>
			Unannealed	Annealed	Assignment
(2985 sh, vs (2978 sh, vs				2985 m	$\nu_{\mathrm{C-H}}$
2974 vvs	2974 vs		2972 s	2973 s	$ u_{\mathrm{C-H}} $
2963 sh, vs	2963 vs		2963 vs	2957 vs	$v_{\mathrm{C-H}}$
2933 vs	2930 sh, m		2925 sh, w	2931 sh, w	$v_{\mathrm{C-H}}$
2925 vs	2921 s		2915 s	2920 vs	$ u_{\mathrm{C-H}} $
2905 s				2906 sh, m	$ u_{\mathrm{C-H}} $
(2885 s 2880 s	2895 sh, m		2885 m	2890 m	$v_{\mathrm{C-H}}$
2875 s	2867 m		2866 m	2865 s	$\nu_{\mathrm{C-H}}$
2855 m				2855 sh, w	
$\sim$ 2840 sh, w	2837 w		2830 vw	2829 vw	
1470 s	1469 sh, w		1468 sh, w	1469 s	$\delta^{ t d}_{ t CH_ullet}$
1460 vs	1462 vs		1462 s	1462 w	$\delta^{ ext{d}}_{ ext{CH}_{f s}}$
1452 vs	1454 vs		(1453 s (1448 sh, w	1452 s	$\delta_{ ext{ iny CH}_ullet}^ ext{d}$
1445 vs	1445 vs		1443 s	1447 s	$\delta^{ ext{d}}_{ ext{CH}_ullet}$
1435 vs	1435 vs		1434 s	1432 s	$\delta^{ ext{d}}_{ ext{CH}_{f a}}$
1428 sh, m	1428 vs		1421 s	1425 s	$\delta^{ t d}_{ t CH_{ullet}}$
1420 sh, w	1420 sh, w			1420 sh, w	
(1397 sh, w 1394 sh, w 1387 s	1383 s	1380 s	(1383 sh, m (1380 m	(1382 sh, m (1380 s	$\delta_{ ext{ iny CH.}}^{ ext{ iny S}}$

<sup>1)</sup> J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp, and G. Waddington, J. Amer. Chem. Soc., 77, 6119 (1955).

<sup>2)</sup> D. W. Scott and M. Z. El-Sabban, J. Mol. Spectrosc., 30, 317 (1969).

Table 1 (Continued)

Gaseous Room Temp.	Liquid Room Temp.	$ ext{CS}_2$ soln. Room Temp.	Solid		
			Unannealed	Annealed	Assignment <sup>b)</sup>
(1378 s 1368 s	1366 s	1365 s	(1367 m 1364 s	(1372 s (1363 s	$\delta_{ ext{ iny CH}_ullet}^{ ext{ iny S}}$
(1329 w 1323 w	1321 w	1319 w	1328 w	1328 vw	
(1316 w 1308 w	1313 w	1312 w	1316 w	1318 m	$\delta_{ ext{CH}_{f s}}^{ ext{s}}$
1285 sh, vw	$\sim$ 1280 sh, vw	$\sim$ 1280 sh, vw	1282 sh, w	_	
1276 sh, w	1275 sh, m	1275 sh, m	1275 w	1276 m	
1270 sh, w 1265 sh, w	1268 sh, m 1263 m	1268 sh, m 1263 s			
(1256 vs (1249 vs (1242 vs	1244 vs	1243 vs	1245 vs	1245 vs	
1230 sh, vw	1229 sh, vw	1227 sh, vw			
(1167 s (1162 s (1155 s	1159 s	1157 s	(1159 s (1155 sh, s	(1161 sh, s (1158 s	
1115 vw	1113 w	1114 w	1113 w	1113 vw	
1108 vvw	1108 sh, vw	1108 sh, vw		_	
(1075 sh, m 1068 m	1064 s	1063 s	1060 s	1059 s	
$\binom{1060 \text{ m}}{1054 \text{ sh, m}}$	1059 s	1057 s	1057 sh, w		
$\sim$ 1025 vvw	1038 sh, vvw	1038 sh, vvw	_		
1015 vvvw	1015 vvw	1015 vvw			
	~990 vvw	~990 vvw	992 vw	994 vw	
075 1	$\sim$ 985 sh, vw	$\sim$ 985 sh, vw	_		
975 sh, w	980 sh, vw	980 sh, vw	000 -1		
970 sh, w 965 m	970 sh, w 965 sh, m	970 sh, w	969 sh, s	966 s	
/958 sh, m		965 sh, m	966 s	900 s	
(955 m	957 s	955 s	959 m		
952  sh, m	952 sh, m	951 sh, m	952 m	952 w	
940 sh, w	941 sh, vw	940 sh, vw	944 sh, vw	945 m	
925 vw	927 w	927 w	927 w	932 m	
920 vw	920 sh, vw	920 sh, vw	921 sh, vvw		
	918 sh, vvw	917 sh, vvw	918 sh, vvw		
885 w, br	884 w	884 w	884 w	884 m	
725 vw	725 w	725 w	727 w	727 m	$ u_{\mathrm{C-S}} $
690 vw	690 vvvw	690 vvvw		-	
647 w 638 w 630 w	637 m	637 m	637 m	638 m	$ u_{\mathrm{C-S}} $
610 vw	610 w	610 w			$\nu_{\mathrm{C-S}}$
	537 vvw, br				<b>.</b> .
	456 vvvw				
	427 vw		426 w	429 w	$oldsymbol{\delta_{\mathtt{skel}}}$
	420 sh, vw		419 sh, vw		
	349 vw		353 vw	$\sim$ 355 vw	$\delta_{ m skel}$
	334 vw		337 sh, vw	338 vw	$\boldsymbol{\delta_{\mathrm{skel}}}$
	327 vw		329 vvw		
	323 sh, vvw		325 sh, vvw		
	276 vvw			-	
	255 vvw				
	234 vvvw		$\sim$ 235 vvw	$\sim$ 235 vvw	$\delta_{ m skel}$
	217 vvw		217 vvw	217 vvw	$\delta_{ ext{skel}}$

s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.
a) Above 3000 cm<sup>-1</sup> and 2800—1500 cm<sup>-1</sup> regions are omitted.
b) ν, stretching; δ<sup>d</sup>, degenerate deformation; δ<sup>s</sup>, symmetrical deformation; δ<sub>skel</sub>, skeletal deformation (including torsions).

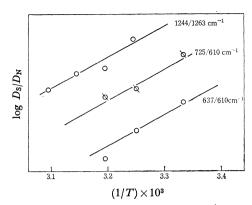


Fig. 1. Plots of  $\log D_{\rm S}/D_{\rm N}$  vs.  $1/T\times 10^3$  of the three liquid-band pairs of methyl isopropyl suifide.  $D_{\rm S}$ : Stable form,  $D_{\rm N}$ : Less stable form.

in the liquid state and five bands remain in the annealed state. Thus, in the liquid or gaseous spectra in the C-S stretching and skeletal deformation regions, there are bands which correspond to two forms. In the annealed state, this sulfide may exist in one form.

In order to confirm the existence of the rotational isomers, we attempted to make an experiment on the solvent effects. We took up the bands at 637 and  $610 \text{ cm}^{-1}$  and used cyclohexane and acetone as the solvents. In this species, however, it seems that the difference in the dipole moment between the two conformations,  $C_8$  and  $C_1$ , is not very much. In the observed spectra, we cannot see any clear difference.

We have, then, tried to determine the temperature dependence of the liquid bands at temperatures of  $27-50^{\circ}\mathrm{C}$ . Figure 1 shows the plots of  $\log D_{\mathrm{S}}/D_{\mathrm{N}}$  vs.  $1/T\times10^3$  of the three liquid-band pairs. In Fig. 1,  $D_{\mathrm{S}}$  means the stable forms and  $D_{\mathrm{N}}$  means the less stable forms. The origin of  $\log D_{\mathrm{S}}/D_{\mathrm{N}}$  is different in each case. The pairs of bands at 1244/1263, 725/610, and at  $637/610~\mathrm{cm}^{-1}$  show nearly the same temperature dependence. From these slopes, we can see the enthalpy difference between two rotational isomers; the order of  $\Delta H$  is evaluated to be ca. 1—1.5 kcal/mol. We cannot, however, determine an exact value, since our obtained data are not sufficient.

From the obtained infrared data, therefore, we can postulate for this sulfide that: a) two conformations coexist in the liquid and gaseous states (energy difference  $\Delta H = 1.5 \text{ kcal/mol}$ ), and b) one form exists in the crystalline state.

## Experimental

The methyl isopropyl sulfide was prepared by the method of McAllan *et al.*,<sup>3)</sup> bp 84—85°C/760 mmHg (reported bp<sup>3)</sup> 84.8°C/760 mmHg). The purity of this sulfide was checked by means of gas chromatography. The methods of infrared recording and instrument used were described previously.<sup>4)</sup>

<sup>3)</sup> D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, J. Amer. Chem. Soc., 73, 3627 (1951).

<sup>4)</sup> M. Ohsaku, Y. Shiro, and H. Murata, This Bulletin, 45, 954 (1972).