

Conformational behaviour and vibrational spectra of 3-methyl 2-butanethiol

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Abstract. The Raman spectra of 3-methyl 2-butanethiol in the temperature range -120°C to $+60^{\circ}\text{C}$ have been recorded together with its liquid phase infrared spectrum at room temperature. The spectral analysis shows that the molecule of the compound exists in the liquid state, in three different rotameric configurations *A*, *B* and *C* of which the form *A* is the stablest. Besides, a tentative assignment of the observed vibrational frequencies arising from the rotameric forms has been presented.

Keywords. Raman spectra; infrared spectra; temperature dependence of Raman band intensities; rotational conformers; energy differences; vibrational experiment.

1. Introduction

Rotational isomerism in substituted alkanes has been studied both experimentally and theoretically. It is now fairly well understood how the different rotameric properties, such as the number of stable rotational conformers, their stabilities and energy differences in these molecules change with the nature, position and number of substituents specially, when the substituents are halogen atoms. However, this is not so if the substituent is a group of atoms like the thiol group. Experimental data on rotational isomerism in alkane thiols and theoretical computations (Freeman 1974) are meagre and far from adequate. Nevertheless, it has been possible to interpret the experimental data by assuming that the rotational conformers in mercaptoalkanes arise mainly due to rotations about the skeletal C-C bonds and that the thiol group remains oriented in a fixed configuration except in the rare case of ethyl mercaptan (Smith *et al* 1968 ; Wilson 1972). But the task of ascertaining how the number of stable rotational isomers and their stabilities depend on the position of the substituent thiol group requires the acquisition of more experimental data in differently-substituted alkanethiols. Accordingly detailed Raman spectroscopic investigations on the vibrational spectrum of 3-methyl 2-butanethiol in the temperature range -120°C to $+60^{\circ}\text{C}$ and the IR spectrum of the same compound in the liquid phase has been studied.

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Results obtained have been compared with the findings reported earlier for other alkanethiols including the two very similar molecules of 2-methyl-1-propanethiol (Ozaki *et al* 1975) and 2-butanethiol (McCullough *et al* 1958). These experimental data together with their discussion form the subject-matter of this paper.

2. Experimental

3-methyl 2-butanethiol from M/s. Schuardt (Germany) was distilled under reduced pressure and its Raman spectrum in the liquid state was obtained both photographically and with a 200 mW 4880 Å radiation of argon ion laser source of a Cary 82 and Spex C laser Raman spectrophotometers. The Raman spectrum in the solid state, the polarisation character of the Raman lines and the temperature dependence of the intensities of some of the Raman lines in the range -120° C to 60° C were studied with the same spectrophotometers. The IR spectrum was recorded in a Perkin Elmer model 21 spectrophotometer with rock salt optics.

3. Results

The Raman and IR frequencies with estimated relative intensities in different phases are given in table 1. The polarisation character of the Raman lines are also shown in the table including the probable assignments of the observed frequencies in terms of the modes of vibration in different rotameric forms of the molecule. The variation in the intensities of Raman lines due to C-S stretching mode of vibration at three temperatures is shown in figure 3.

4. Discussions

4.1. Rotameric forms and their stabilities

If the CH_3 groups are considered rigid and the SH group given a fixed orientation the molecule of 3-methyl 2-butanethiol will have only one central C-C axis of rotation. The three rotational conformers arising due to orientation about this bond are shown in figure 1 and are indicated as *A*, *B* and *C*. It may be noted that while in form *C*, the thiol group is in the trans-position with respect to the hydrogen atom, in forms *A* and *B* they are gauche with respect to each other.

The configuration of these rotamers is very similar to that obtained in 2-butanethiol in which there is a H-atom in place of one of the two CH_3 groups in the *second* carbon atom. These forms shown in figure 2 have energies, according to McCullough *et al* (1958), in the order $E_C > E_B \gg E_A$. From a comparison of these three rotameric forms with those of 3-methyl 2-butanethiol and considerations of the nonbonded interactions in the various groups in the different conformers of the two molecules the energies of the three conformers of 3-methyl 2-butanethiol are found to be $E_B > E_C > E_A$ in the free state. The three rotamers will have approximately the same dipole moment and lowering of energy in the liquid phase is not expected to change the relative energy differences significantly. In other words, the form *A* will be the most stable and with lowering of temperature the intensity of the Raman bands due to this form would increase relative to that

Table 1. Raman and infrared bands of 3-methyl 2-butanethiol.

IR bands (cm ⁻¹) liquid (thin film)	Raman shifts (cm ⁻¹)		Assignment	Rotamer
	Liquid	Glassy mass (-120 °C)		
	109 (3)		C-C torsion	
	133 (1)		C-C torsion	
	225 (4) D	absent	C-C-S deformation	B/C
	320 (3) D	320 (2)	C-C-S deformation	A
	358 (5) P	absent	C-C-C deformation	B
	425 (5) P	425 (2)	C-C-C deformation	B/C
	483 (6) P	483 (3)	C-C-C deformation	B/C
	513 (4) P	513 (5)	C-C-C deformation	A
	623 (5) P	623 (8)	C-S stretch	A
	650 (10) P	650 (6)	C-S stretch	C
	680 (8) P	680 (5)	C-S stretch	B
780 (w)	786 (6) D	786 (10)	CSH angle deformation	A
870 (w)	872 (3) P	872 (3)	CSH angle deformation	B/C
900 (w)	915 (5) P	915 (4)	CH ₃ rock	B
960 (w)	960 (3) D	960 (3)	CH ₃ rock	C
	990 (3) D	990 (4)	C-C stretch/CH ₃ rock,	A
1015 (m)	1015 (1) P	absent	C-C stretch	B/C
	1030 (2) D	1030 (4)	C-C stretch	A
1080 (m)	1080 (3) P	1080 (2)	C-C stretch/CH ₃ rock	B/C
1110 (w)	1115 (3) D	1115 (4)	CH ₃ Rock	A
1150 (m)	1152 (3) D	1152 (5)	C-C stretch	A
	1188 (3) P	1188 (5)	C-C stretch	A
1235 (m)	1237 (5) P	1237 (4)	CH deformation	B/C
	1260 (2) D	1260 (4)	CH deformation	A
	1290 (3) P	1290 (3)	CH deformation	B/C
1330 (m)	1326 (3) D	1326 (5)	CH wagg	A
	1343 (2) D	1343 (2)	CH wagg	B/C
1360 (ssh)				
1370 (s)	1368 (1) P	1368 (2)	(CH ₃) bend sym.	
1390 (ssh)	1388 (2) P	1388 (2)		
1455 (vs)	1454 (8) D	1454 (8)	(CH ₃) def. asym.	
	1472 (7) D	1472 (8)		
2570 (m)	2569 (9) P	2569 (9)	(S-H) stretch	
2880 (s)	2860 (10) P	2860 (10)	(CH) ₂ of CH ₃ stretch	
2930 (ssh)	2910 (10) P	2910 (10)	(CH) of CH stretch	
2960 (vs)	2958 (5) D	2958 (9)	(CH) ₃ of CH ₃ stretch	

P, polarised ; D, depolarised ; s, strong ; m, medium ; w, weak ; v, very ; sh, shoulder.

due to the two others. On this basis the Raman bands in table 1 has been assigned to the rotamer A and are so indicated.

It is seen from table 1 that there are three polarised Raman bands at 623, 650 and 680 cm^{-1} in the spectrum of 3-methyl 2-butanethiol. They correspond to the three frequencies 620, 659 and 684 cm^{-1} in 2-butanethiol which have been assigned to the C-S stretching vibrations in the three rotamers of the molecule by McCullough *et al* (1958). The former three Raman bands, by analogy, represent the ν (C-S) frequencies in the three rotamers of the present molecule. It is seen from figure 3 that the relative intensities of the three bands vary with change of temperature and this change is the largest for the band at 623 cm^{-1} . The intensity of this band increases appreciably with lowering of temperature and therefore, it is attributed to the most stable rotamer (A) of the molecule. The observed variation in the intensities of the Raman bands 650 and 680 cm^{-1} suggest their origin to forms C and B respectively. From plots of the variation of $\log I_{623}/I_{650}$ and $\log I_{623}/I_{680}$ against reciprocal of absolute temperature (figures 4, 5) the energy differences ΔE are obtained as 0.25 and 0.49 kcal/mol. It is seen that form C is more stable than form B by 250 cal/mol. This reasonably confirms the existence of three rotameric forms as assumed in the very beginning.

4.2. Assignment of the vibrational frequencies

4.2a. *Group vibrations*: The molecule of 3-methyl 2-butanethiol with 18 atoms will have 48 modes of vibration and 48 vibration frequencies. These may be classified roughly in terms of vibrations of the methyl groups, the C-H group, the CSH group and skeletal modes. To each of the three methyl groups, there belongs three C-H stretchings, three CH deformations, two CH_3 rocking and one $\text{H}_2\text{C}-\text{C}$ torsional modes of vibrations. The CH group will give rise to on

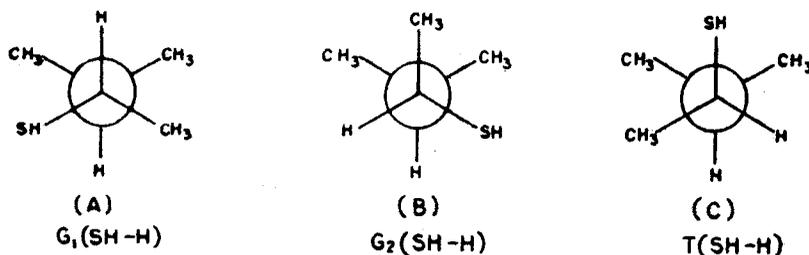


Figure 1. Three rotational conformers in 3-methyl 2-butanethiol.

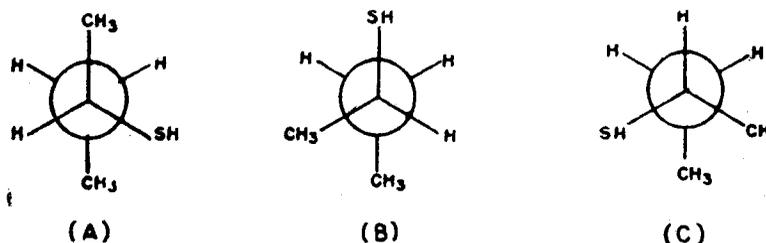


Figure 2. Three possible isomers in 2-butanethiol.

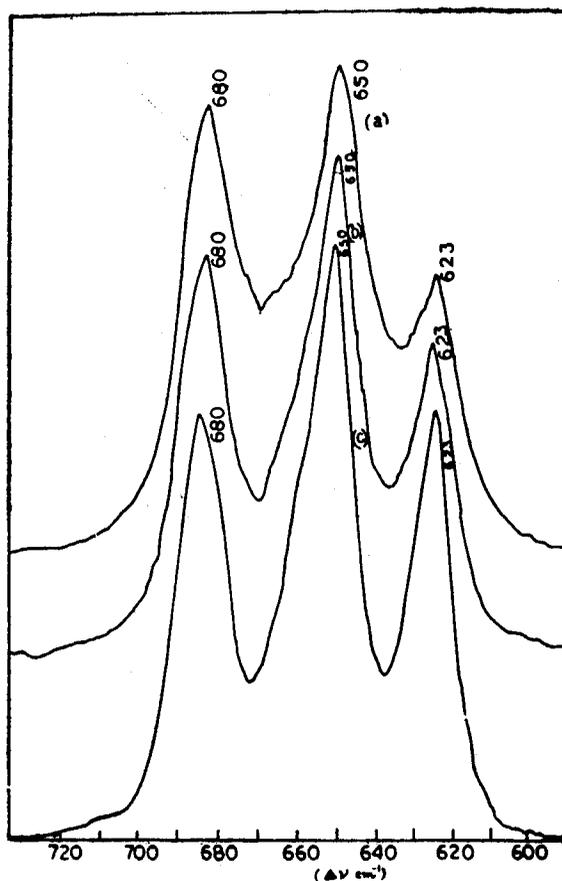


Figure 3. Variations in the intensities of Raman lines due to C-S stretching modes of vibration of 3-methyl, 2-butanethiol. (a) 333 K, (b) 260.5 K, (c) 213 K.

CH stretching and two CH deformation modes while there will be one S-H stretching vibration, one CSH angle deformation and one CS torsional mode for the SH group. The assignment of most of these modes is straightforward and is not given here. However, it is difficult to assign the vibrations arising from the torsional modes. Further, difficulties are experienced in separating the CH_3 rocking modes from those arising from C-C skeletal stretching vibrations. These are considered in the next section.

4.2b. *Skeletal vibrations*: The skeletal of 3-methyl 2-butanethiol molecules gives rise to 12 vibrational frequencies in each rotamer and they may be broadly classified as C-C torsion (1), C-C-S deformations (2), C-C-C deformations (3), C-C stretching (4), and C-S stretching (1). All these vibrations are sensitive to the configuration of the rotamers. Some of their assignments are discussed below.

The two low frequency Raman bands 109 and 133 cm^{-1} observed in the Raman spectrum of the liquid at room temperature are believed to arise from torsional vibrations but their assignments are not definite. In most mercapto alkanes there appear two Raman bands in the frequency region 200-350 cm^{-1} , attributed to

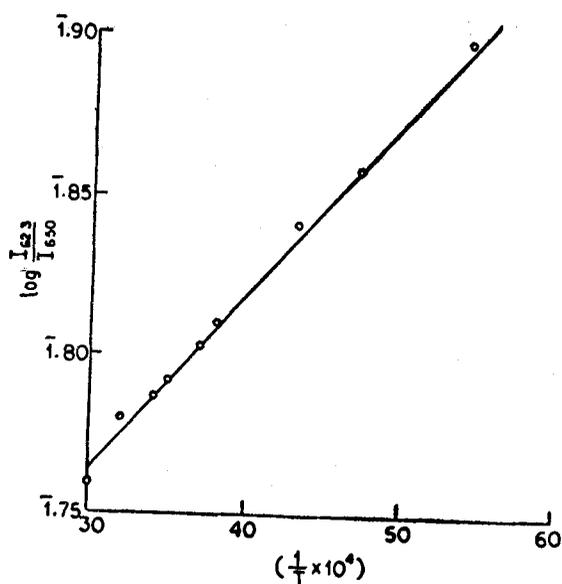


Figure 4. Plot of $\log I_{623}/I_{650}$ vs. $1/T$.

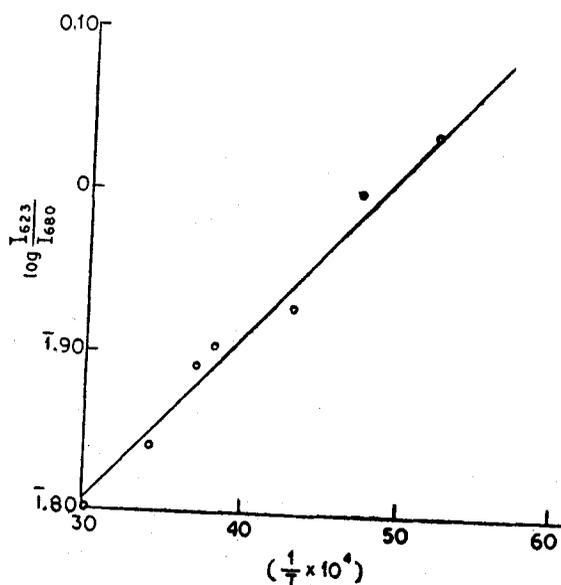


Figure 5. Plot of $\log I_{623}/I_{680}$ vs. $1/T$.

C-C-S deformation vibration. In the present molecule, the two frequencies 225 and 320 cm^{-1} most probably represent this mode of vibration. Since with lowering of temperature, the former vanishes and there is little change of intensity in the latter, the frequency 225 cm^{-1} corresponds to the least stable of the forms *B* and *C* while the latter represents one of the two δ (C-C-S) modes due to form *A*.

Several Raman bands are found to appear in the frequency interval $350\text{--}500 \text{ cm}^{-1}$ and their number depend on the number of carbon atoms in the skeleton. Previous workers have attributed these vibrations to skeletal C-C-C deformations.

Accordingly the polarised Raman bands 358, 425, 483 and 513 cm^{-1} observed in the liquid phase spectrum of 3-methyl 2-butanethiol are assigned to this mode of vibration. It may be noted that these bands strikingly correspond to the frequencies 377, 412, 453 and 517 cm^{-1} assigned to $\delta(\text{C-C-C})$ mode in 2-butanethiol by McCullough *et al* (1958). The first of these bands vanishes at low temperature and should be attributed to the least stable form, the other two bands whose intensities decrease appreciably on cooling should correspond to the forms *B* or *C*. The intensity of the band 513 cm^{-1} , on the other hand, slightly increases at low temperature and thus is attributed to form *A*. Though not all the possible twelve frequencies due to $\delta(\text{C-C-C})$ modes in the rotamers have been recorded, the presence of Raman bands whose intensities vary differently with lowering of temperature confirms the presence of at least two rotamers. From a plot of $\log I_{513}/I_{483}$ against $1/T$ (figure 6) the energy difference between the conformers *A* and *B* or *C* or both, is obtained as 0.34 kcal/mol, which is roughly the average of the energy difference values between (i) forms *A* and *B*, and (ii) forms *A* and *C*, obtained from the temperature dependence of Raman bands due to C-S stretching modes of vibration.

The frequencies due to C-S stretching vibrations have already been discussed and those due to C-C skeletal stretching are now considered. As with the $\delta(\text{C-C-C})$ modes, in this case also we should expect twelve C-C stretching vibrations appropriate to the three rotamers. From the data obtained from published literature, the Raman bands in the frequency region 900–1200 cm^{-1} are believed to arise from C-C stretching modes. However, where there are methyl groups in the molecule, the two CH_3 -rocking modes appear respectively in the region 850–1000 cm^{-1} and at about 1100 cm^{-1} , which makes reliable assignment of the $\nu(\text{C-C})$ frequencies difficult. The frequencies 915, 960, 990, 1015, 1030, 1080, 1115, 1152 and 1183 cm^{-1} observed in the vibration spectra of 3-methyl 2-butanethiol certainly represent the two CH_3 -rocking modes and C-C stretching modes of

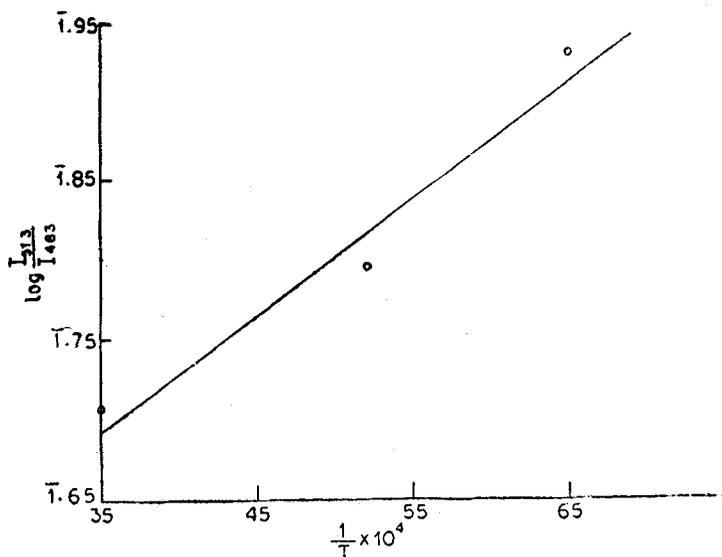


Figure 6. Plot of $\log I_{513}/I_{483}$ vs. $1/T$.

vibrations in the three rotamers. Of these 1152 and 1183 cm^{-1} definitely belong to ν (C-C) mode and since their intensity increases when the temperature is lowered they are associated with the rotamer A. From a comparison with the ν (C-C) frequencies observed in 1,2,ethanedithiol, 1,3 propanedithiol and 2-mercapto-ethanol (Hayashi *et al* 1965; Nandy *et al* 1973a, b; Som *et al* 1975) where there are no complications arising from CH_3 rocking modes of vibration, the Raman bands 1015 and 1030 cm^{-1} are assigned to the ν (C-C) vibrations, the former belonging to the less stable forms B or C and the latter to form A. In view of the CH_3 rocking frequencies proposed for 2-methyl 1-propanethiol (Ozaki *et al* 1975; Scott *et al* 1958) and 2-butanethiol (McCullough *et al* 1958), the bands 915, 960 and 1115 cm^{-1} may be reasonably assigned to this mode in the three rotamers as shown in table 1. The two Raman bands 990 and 1080 cm^{-1} may arise from either R (CH_3) or ν (C-C) modes but their assignment is not certain.

Some comments on the C-S-H deformation frequencies of 3-methyl 2-butanethiol are in order. In different alkanethiols the frequencies corresponding to these modes have variously been put in the frequency interval 775 to 900 cm^{-1} . For example Ozaki *et al* (1975) has assigned the Raman band at 774 cm^{-1} in 2 methyl 1-propanethiol to δ (C-S-H) modes while Torgriksen and Klæboe (1970) has proposed for this mode two Raman frequencies 778 and 814 cm^{-1} in 1-propanethiol. In 1-2 ethanedithiol (Hayashi *et al* 1965), the two modes are at 800 and 890 cm^{-1} and McCullough *et al* (1958) have attributed the frequency 863 cm^{-1} to the δ (C-S-H) mode in 2-butanethiol. Following these observations the two Raman frequencies 786 and 872 cm^{-1} observed with the present molecule are assigned to the CSH angle deformation mode. Since the intensity of 786 cm^{-1} Raman band increases at low temperature it certainly originates from the most stable A rotamer.

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