

Infrared spectra and normal vibrations of O-methyl monothiocarbonate, S-methyldithiocarbonates and N-methylmonothiocarbamates, methyltrithiocarbonate, and related ions

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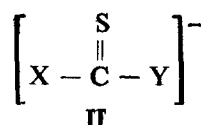
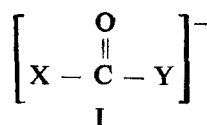
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Abstract. Infrared spectra and normal vibrations of ions of the type $\begin{matrix} \text{O} \\ || \\ \text{X}-\text{C}-\text{Y} \end{matrix}$ and $\begin{matrix} \text{S} \\ || \\ \text{X}-\text{C}-\text{Y} \end{matrix}$, with X and Y as S, O and N have been compared and discussed.

Keywords. Infrared spectra; thiocarbonates; trithiocarbonates; monothiocarbamates; normal vibration analysis.

1. Introduction

It is well known that the stretching frequency of C=O bond reaches a limiting value in the carboxylate ion due to the presence of the two equally important canonical structures (Rao 1963). We have been interested in the study of the vibrational spectra of various organic carbonate and thiocarbonate ions, in order to understand the nature of their normal vibrations and environmental effects on them. In this paper, we report the infrared spectra and normal vibrations of ions of the general formula I and II,



where X and Y can be O, S or N. Specifically, we have investigated the infrared spectra of S-methyldithiocarbonate (I, X=Y=S), N-methylmonothiocarbamate (I, X=N, Y=S) and methyltrithiocarbonate (II, X=Y=S) and discussed their

normal vibrations in comparison with those of related molecules. The results of the study have enabled interesting spectra-structure correlation in the related series of ions of the types I and II.

2. Experimental

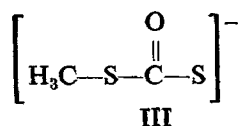
Potassium S-methyldithiocarbonate was prepared by the action of COS on potassium methyl mercaptan in cold. Potassium methyl mercaptan was prepared by the action of methyl mercaptan (Arndt 1921; Shildneck and Wallace 1932; Backer and Stedhouder 1933; Shildneck and Wallace 1934) on KOH dissolved in a minimum quantity of water and excess of CH₃CN. Potassium O-methylmonothiocarbonate was prepared by the action of COS on ice-cold potassium methoxide. Potassium S-methyldithiocarbonate was prepared by the action of CS₂ on potassium methyl mercaptan kept in a freezing mixture. Methylammonium salt of N-methylthiocarbamate was prepared by the action of methylamine on COS, the reaction being carried out by passing the two gases simultaneously into pure, cold dry ether. Dimethyl-ammonium salt of N-N dimethyl-thiocarbamate was prepared by the action of dimethylamine on COS, the two gaseous reactants being simultaneously led into pure, cold, dry ether.

Infrared spectra were recorded with a Perkin Elmer Model 580 spectrophotometer. Spectra were recorded in Nujol mull as well as in KBr pellet. Normal vibration calculations were made using an IBM 360/44 computer, employing the Urey-Bradley force field.

3. Results and discussion

3.1. S-methyldithiocarbonate ion

The important infrared bands of S-methyldithiocarbonate ion, III,



are listed in table 1. Although we have shown the double bond to be localised on the CO group, it should be noted, that the other canonical form, with the double bond on the thiocarbonyl group is equally important. As such, we would expect a C=O stretching frequency considerably lower than in ordinary ketones and esters and a C-S stretching frequency higher than that due to a C-S single bond. Accordingly, we find, that the C=O and C-S stretching frequencies are at 1600 and 950 cm⁻¹ respectively. It is interesting to compare the normal modes of III with those of O-methylmonothiocarbonate ion, IV.

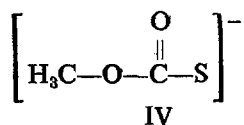


Table 1. Comparison of the infrared band assignments of S-methyldithio and O-methylmonothiocarbonate ions.

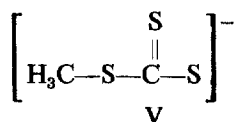
$\left[\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{S}-\text{C}-\text{S} \end{array} \right]^-$ III		$\left[\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{O}-\text{C}-\text{S} \end{array} \right]^-$ IV		
cm ⁻¹	Assignment	cm ⁻¹	Assignment	
3010	$\nu_{as}(\text{CH}_3)$	3020	$\nu_{as}(\text{CH}_3)$	
2940	$\nu_s(\text{CH}_3)$	2940	$\nu_s(\text{CH}_3)$	
1600	$\nu(\text{C}=\text{O})$	1560	$\nu(\text{C}=\text{O})$	
1400 } 1390 } 1350 }	$\delta(\text{CH}_3)$	1456 } 1438 } 1416 }	$\delta(\text{CH}_3)$	
..		1339		815 + 532
1180		$\rho(\text{CH}_3)$		1188
1135	655 + 498	
..	..	1090	$\rho_{as}(\text{COC}) + \rho(\text{SCO})$	
1000	498 × 2	1048	532 × 2	
950	$\nu(\text{CS})$	965	$\nu_s(\text{COC}) + \nu(\text{CS})$	
780	$\nu_{as}(\text{CSC})$	812	$\nu_s(\text{COC}) + \delta(\text{COC})$	
655	$\nu(\text{CSC})$	
625	$\gamma(\text{SCOS})(A'')$	695	$\gamma(\text{OCSO})(A'')$	
498	$\nu(\text{CS}) + \delta(\text{SCO})$	532	$\nu(\text{CS}) + \delta(\text{SCO})$	
485	$\delta(\text{SCO}) + \delta(\text{CSC})$	423	$\delta(\text{SCO})$	
270	$\rho(\text{SCO}) + \delta(\text{CSC})$	301	$\rho(\text{SCO}) + \delta(\text{COC})$	

ν = Stretching; δ = bending; ρ = rocking; γ = out of plane bending; s = symmetric; as = asymmetric

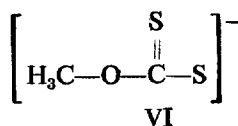
Infrared spectrum and normal vibrational analysis of IV have been discussed by Mattes and Scholten (1975). We find that by incorporating slight changes in the force constants of IV, the spectrum of III can be readily reproduced. The important force constants used for IV are: $k(\text{C} \equiv \text{O}) = 10$, $k(\text{C} \equiv \text{S}) = 3.8$ and $k(\text{C} - \text{S}) = 3.5$ m dyn/Å. The other force constants are similar to those of IV and related compounds. We have compared the infrared band assignments of III and IV in table 1. It can be readily seen that the spectra are quite similar. Instead of the COC asymmetric and symmetric modes of IV in the 1090–812 cm⁻¹ region, we find the corresponding modes of CSC in III, in the region 780–650 cm⁻¹. The $\gamma(\text{OCSO})(A'')$ band at 695 cm⁻¹ in IV, finds a corresponding band due to $\gamma(\text{SCOS})$ in III. All the bands between 500–300 cm⁻¹ in III and IV are also similar, the bands appearing at slightly lower frequencies in III. It is interesting that the band attributable to C \equiv O stretch, is lower in IV compared to III. It appears that the bond order of the carbonyl group in the anion is reduced, when it is bound to an oxygen atom more than when it is bound to a sulphur atom.

3.2. Methyltrithiocarbonate ion

The major infrared bands of methyltrithiocarbonate ion, V,



are listed in table 2. In this ion, we have the dithiocarboxylate group and we should therefore find the asymmetric and symmetric stretching of the CS_2^- group, just as in CO_2^- of carboxylates. We see bands in the region $1180-950 \text{ cm}^{-1}$ which can be ascribed to these modes. We also see the asymmetric and symmetric CSC stretching bands similar to those found in the S-methyldithiocarbonate ion, III. In table 2, we have compared the infrared bands of V, with those of O-methyldithiocarbonate ion, VI,



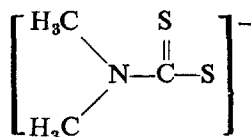
which also has the CS_2^- grouping. The similarities in the band positions are quite evident. The $\gamma(\text{CS}_2)$ (A'') modes in both these compounds, appear around 575 cm^{-1} . The COC stretching bands of VI, are comparable to those found in the O-methylmonothiocarbonate ion, IV. Since the normal vibrational analysis of O-methyldithiocarbonate ion, VI, has been carried out by Mattes and Pauleikhoff (1973), we

Table 2. Comparison of the infrared band assignments of methyltrithiocarbonate and O-methyldithiocarbonate ions.

$\left[\begin{array}{c} \text{S} \\ \\ \text{H}_3\text{C}-\text{S}-\text{C}-\text{S} \end{array} \right]^-$ V		$\left[\begin{array}{c} \text{S} \\ \\ \text{H}_3\text{C}-\text{O}-\text{C}-\text{S} \end{array} \right]^-$ VI	
cm^{-1}	Assignment	cm^{-1}	Assignment
1180	$\nu_{\text{as}}(\text{CS}_2) + \rho(\text{CH}_3)$	1183	$\nu_{\text{as}}(\text{CS}_2) + \rho(\text{CH}_3) + \delta(\text{COC})$
1110	$\nu_{\text{as}}(\text{CS}_2) + \rho(\text{CH}_3)$	1110	$\nu_{\text{as}}(\text{CS}_2) + \rho(\text{CH}_3)$
1055	$\nu_s(\text{CS}_2) + \delta(\text{CS}_2)$	1045	$\nu(\text{COC}) + \nu_s(\text{CS}_2)$
940	$\nu_s(\text{CS}_2) + \nu(\text{CSC}) + \delta_s(\text{CH}_3)$	944	$\nu(\text{COC}) + \nu_s(\text{CS}_2)$
720	$\nu_{\text{as}}(\text{CSC})$
670/620	$\nu_s(\text{CSC})$	620	$\nu_s(\text{CS}_2) + \delta(\text{COC})$
570	$\gamma(\text{CS}_2) (A'')$	580	$\gamma(\text{CS}_2) (A'')$
470	$\nu_s(\text{CS}_2) + \delta(\text{CSC})$	477	$\delta(\text{COC}) + \nu_s(\text{CS}_2)$
330	$\delta(\text{CS}_2)$	337	$\delta(\text{CS}_2)$
290	$\delta(\text{CSC})$	270	$\gamma(\text{COC}) (A')$

could calculate, with fair agreement, the vibrational modes of methyltrithio-carbonate ion, V, by minor modification of force constants. The two important force constants of V are: $k(C \equiv S) = 3.95$ and $k(C-S) = 3.5$ mdyn/A.

We are in a position to compare the infrared bands of V and VI with the bands reported by Jensen *et al* (1971) for N,N-dimethyldithiocarbamate ion, VII.

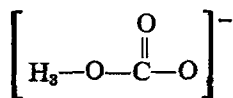


VII

In VII, we find the asymmetric and symmetric stretching bands of CS_2^- in the region $1257-965 \text{ cm}^{-1}$, showing thereby that the CS_2^- stretching modes vary in the order,

$$\text{NCS}_2^- > \text{OCS}_2^- \approx \text{SCS}_2^-.$$

The other bending and stretching modes of VII are similar to those of the N-methyl-monothiocarbamate ion which is discussed later in this paper. It is also interesting to compare the infrared spectrum of V with that of methylcarbonate ion, VIII, reported by Mattes and Schölten (1975).

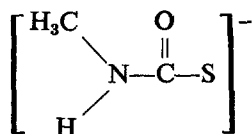


VIII

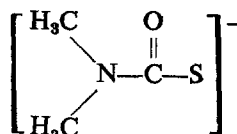
Infrared spectrum of VIII shows asymmetric and symmetric stretching frequencies of CO_2^- respectively at 1680 and 1310 cm^{-1} ; the COC asymmetric and symmetric stretching frequencies are observed at 1080 and 893 cm^{-1} respectively. The stretching modes of CO_2^- in VIII, are at considerably higher frequencies than those found of COS^- group discussed earlier.

3.3. *N-methyl and N,N-dimethylmonothiocarbamate ions*

We have studied the infrared spectra of N-methylmonothiocarbamate ion, IX and N, N-dimethylmonothiocarbamate ion, X.



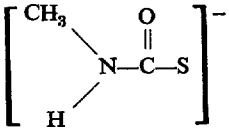
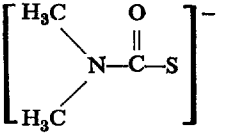
IX



X

The spectrum of IX should have characteristic bands of secondary amides (Rao 1963), in addition to those of the COS group. Accordingly, we are able to assign all the amide bands (amides I to VI) for this compound (table 3). The only difficulty is in the assignment of the amide V band (out-of-plane NH bend) which

Table 3. Comparison of the infrared band assignments of N-methyl and N, N-dimethyl monothiocarbamate ions.

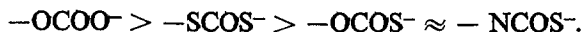
			
cm ⁻¹	Assignment	cm ⁻¹	Assignment
1570 } sh	Amide I ^(a) +	1565 } sh	$\nu(\text{C}=\text{O}) + \nu(\text{C}-\text{N})^{(a)}$
1525 }	Amide II	1520 }	
1020	$\nu_{as}(\text{CNC})$	1030	$\nu_{as}(\text{CNC})$
990	$\nu(\text{CS})$	990	$\nu(\text{CS})^{(b)}$
965	$\nu_s(\text{CNC}) + \nu(\text{CS})$	930	$\nu(\text{CNC})$
830	$\nu_s(\text{CNC}) + \delta(\text{CNC})$	825	$\nu(\text{CNC})$
725	Amide V or $\gamma(\text{NCOS})$ (A ^u)	700	$\gamma(\text{NCOS})$
660	Amide IV
580	Amide VI	615	$\delta(\text{NCO})$
515	$\nu_s(\text{CS}) + \delta(\text{SCO})$	535	$\nu(\text{CS}) + \delta(\text{SCO})$
425	$\delta(\text{SCO})$	415	$\delta(\text{SCO})$
300	$\rho(\text{SCO}) + \delta(\text{CNO})$	300	$\rho(\text{SCO}) + \delta(\text{CNC})$

(a) These are broad bands and could essentially be considered as $\text{C} \cdots \text{O} + \text{C} \cdots \text{N}$ stretching modes; N—H in plane bending would contribute to this band in IX.

(b) This is the stretching mode of the $\text{C} \cdots \text{S}$ band in the monothiocarbamate ion.

appears close to the band position expected of $\gamma(\text{NCOS})$ mode (A^u). We see the CNC stretching modes in the region 1020–830 cm^{-1} . The low frequency bands between 550–300 cm^{-1} are similar to those found in O-methylmonothio and S-methyldithiocarbonate ions.

The infrared bands of N,N-dimethylmonothiocarbamate ion, X, are also shown in table 3. The assignments of many of these bands are similar to those for IX except that the band at 700 cm^{-1} will be $\gamma(\text{NCOS}^-)$, since there can be no amide V band. It is interesting that in both IX and X, the amide I band, due to $\text{C}=\text{O}$ stretch appears around 1570 cm^{-1} , a frequency close to that in some of the other thiocarbonate ions studied by us. The CO stretching frequencies in the three thiocarbonate of the general formula $\text{XC}(\text{O})\text{Y}$ ions studied by us vary in the order,



The present study of the infrared spectra of O-methyl, S-methyl and N-methylthiocarbonate derivatives has yielded interesting comparisons of vibrational frequencies and force constants. The study shows that the Urey–Bradley force constants in such derivatives are transferable. In table 4, we have presented a comparative table of the important stretching frequencies in related series of thiocarbonates, monothiocarbamates and dithiocarbonates. Table 4 clearly shows how the

Table 4. Infrared bands of related series of $\left[\begin{array}{c} \text{O} \\ || \\ \text{X}-\text{C}-\text{Y} \end{array} \right]^-$ and $\left[\begin{array}{c} \text{S} \\ || \\ \text{X}-\text{C}-\text{Y} \end{array} \right]^-$ ions.

$\left[\begin{array}{c} \text{O} \\ \\ \text{X}-\text{C}-\text{Y} \end{array} \right]^-$		$\nu(\text{C}=\text{O})$ cm^{-1}	$\nu(\text{C}-\text{S})$ cm^{-1}	$\nu(\text{C}-\text{X}-\text{C})$ cm^{-1}	$\gamma(\text{X}-\text{C}-\text{O}-\text{Y})$ cm^{-1}
X	Y				
O	S	1560 (10.7)	965 (38%) (3.8)	1090, 965, 812	695
S	S	1600 (10.8)	950 (3.8)	780, 655	625
N	S	1570	990	1020, 965, 830	700
O	O	1680 (asym.); 1310 (sym.) (9.3)		1080, 893	826

$\left[\begin{array}{c} \text{S} \\ \\ \text{X}-\text{C}-\text{Y} \end{array} \right]^-$		$\nu(\text{C}=\text{S})$ cm^{-1}	$\nu(\text{C}-\text{X}-\text{C})$ cm^{-1}	$\gamma(\text{X}-\text{C}-\text{S}-\text{Y})$ cm^{-1}
X	Y			
O	S	1183, 1110, 620 (3.95)	1045, 944	580
S	S	1180, 1110, 1055, 940 (3.95)	720, 620	570
N	S	1257, 1054, 966 (3.95)	1134, 945, 583	590
O	O ^(b)	965 (3.8)	1090, 965, 812	695

(a) Values in brackets are the stretching force constants (mdyne/Å).

(b) This is the same as $\begin{array}{c} \text{O} \\ || \\ \text{X}-\text{C}-\text{X} \end{array}$ with X=O and Y=S.

observed frequencies and calculated force constants are quite similar in these related compounds.

Acknowledgements

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