445. *The Identification of* C=S *Absorptions in the Infrared by Solvent Studies.*

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The C=S group frequency has been identified in a number of compounds through the characteristic behaviour it shows in a range of different solvents. It falls near 1080 cm.$^{-1}$ in cyclic trithiocarbonates, near 1200 cm.$^{-1}$ in dithio-esters, and near 1000 cm.$^{-1}$ in some thioamides. The method is not applicable in compounds in which the C=S link has a very low polarity.

Many workers have attempted the assignment of group frequencies to the C=S link in various environments. Early studies by Sheppard [1] and by Bellamy [2] were inconclusive, possibly because some of the simpler compounds examined exist in polymeric forms. Later work on larger molecules has led to a number of different assignments. Some of these, such as that for the dithio-esters at 1200 cm.$^{-1}$ and for thiocarbonyl chloride [3] at 1180 cm.$^{-1}$, seem to be reasonably well established, but with others such as the thioamides assignments range from 1430 to 830 cm.$^{-1}$. It has also been pointed out [4] that the various assignments are not parallel to those of the carbonyl group in a number of cases. Thus it is surprising to find the C=S frequency in thioamides generally quoted as falling near to or even higher than that in the corresponding thioketones. Similarly, the frequency of thiocarbonyl chloride is very low in relation to that for dithio-esters for example.

In an attempt to resolve some of these anomalies we decided to examine the spectra of a series of C=S compounds in a wide range of different solvents. It has recently been shown that X=O dipoles all tend to exhibit a common pattern of solvent behaviour such that the $\Delta\nu/\nu$ values of any one compound in a series of different solvents can be plotted against the corresponding values of any other to give a straight line.[5,6] Further, when the X=O bond is the only major polar group present it generally shows the only absorption which is at all solvent-sensitive.

It therefore seemed that a study of this kind might well enable some of the C=S assignments to be confirmed unequivocally, whilst also providing a convenient method of assessing the general applicability of the solvent method to problems of this kind.

Experimental

The spectra were measured with a Grubb–Parsons G.S.2 double-beam spectrometer fitted with a 2400 line/inch N.P.L. grating.

Thioacetamide, mercaptobenzothiazole, and tetramethylthiuram monosulphide, obtained commercially, were purified by recrystallisation. Ethyl and n-butyl dithioacetate were prepared by the procedure of Marvel *et al.*[7] Thiobenzophenone was prepared by the standard method.

We are grateful to Dr. J. C. D. Brand for samples of methyl α-dithionaphthoate and thio-α-naphthophenone.

Results.—Our assignments for the C=S absorptions in a number of different compounds are given in the Table, which also shows the changes which occur on passing from one solvent to another. The basis on which each of these assignments has been made is discussed individually below.

(a) *Dithio-esters.* There seems to be reasonably good agreement on the position of the

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[1] Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429.

[2] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 2nd Edn., 1958, p. 355.

[3] Haszeldine and Kidd, *J.*, 1955, 3871.

[4] Bellamy, in " The Organic Chemistry of Sulphur Compounds," Pergamon Press, to be published shortly.

[5] Bellamy and Williams, *Trans. Faraday Soc.*, 1959, **55**, 14.

[6] Bellamy, Conduit, Pace, and Williams, *Trans. Faraday Soc.*, 1959, in the press.

[7] Marvel, Radzitsky, and Brader, *J. Amer. Chem. Soc.*, 1955, **77**, 5997.

C=S bands in these compounds. Bak, Hansen-Nygaard, and Petersen[8] record a common absorption in the range 1225—1190 cm.$^{-1}$ in 21 closely related compounds. Marvel, Radzitsky, and Brader[7] find a slightly lower range, 1190—1170 cm.$^{-1}$, in four others of a different type, whilst Mecke, Mecke, and Lüttringhaus[9] have studied cyclic materials, in which the frequencies are likely to be rather different, and find values near 1050 cm.$^{-1}$. We therefore commenced our study with compounds of this type to confirm the assignments and to establish the applicability of the method.

Ethylene trithiocarbonate was first examined. In the range of solvents listed only one band in the spectrum of this compound showed any change. In agreement with the assignment by Mecke *et al.* this was the band at 1087 cm.$^{-1}$ (n-hexane). The solvent pattern was the same as that of other typical X=O dipoles, so a good straight line plot was obtained when the $\Delta\nu/\nu$ values were plotted against the corresponding values of acetophenone (see Figure). These two facts taken together provide very strong evidence for the assignment of this band to the C=S group.

	Ethyl dithioacetate		n-Butyl dithioacetate		Ethylene trithiocarbonate		T.M.T.S.*	Thioacetamide	
Solvent	$\nu_{C=S}$ (cm.$^{-1}$)	$10^3\Delta\nu/\nu$	$\nu_{C=S}$ (cm.$^{-1}$)	$10^3\Delta\nu/\nu$	$\nu_{C=S}$ (cm.$^{-1}$)	$10^3\Delta\nu/\nu$	$\nu_{C=S}$	$\nu_{C=S}$	δ_{NH}
(Vapour)	1204		1204		1099		—	—	—
Hexane	1199	4·2	1200	3·3	1087	10·9	—	—	—
Cyclohexane	1199	4·2	1199	4·2	1086	11·8	—	—	—
Et$_2$O	1198	5·0	1199	4·2	—		968	980	1643
Decalin	1198	5·0	1199	4·2	1084	13·6	—	—	—
C_2Cl_4	1198	5·0	1198	5·0			968	—	—
Limonene	1197	5·8	1197	5·8			—	—	—
CCl_4	1197	5·8	1197	5·8	1083	14·6	967	—	—
Toluene	1197	5·8	1197	5·8			966	—	—
CS_2	1195	7·5	1195	7·5	1079	18·2	966	—	—
Benzene	1196	6·6	1196	6·7	1078	19·1	965	—	—
Dioxan	1195	7·5	1195	7·5			965	980	1643
MeI	—	—	—	—	1075	21·8	964	—	—
MeCN	1195	7·5	1195	7·5	1075	21·8	964	974	1635
(Liquid)	1195	—	1195	—	—	—	—	—	—
$(CH_2Cl)_2$	—	—	—	—			964		
MeNO$_2$	1194	8·3	1194	8·3			963		
CH_2Cl_2	—	—	—	—	1074	22·7	964	969	1614
$CHCl_3$	—	—	—	—	1075	21·8	963	968	1611
CH_2Br_2	—	—	—	—	1072	24·6	962		
$(CHCl_2)_2$	—	—	—	—	1072	24·6	962	966	—
$CHBr_3$	1193	9·1	1193	9·1	1070	26·4	961	964	1609
$(CHBr_2)_2$	1192	10·0	1192	10·0	1069	27·3	961		
CH_2I_2	1191	10·8	1191	10·8			959		

* T.M.T.S. = Tetramethylthiuram monosulphide.

Ethyl and n-butyl dithioacetate were also studied. Here also only one band in each case was sensitive to solvent changes, and each behaved like a typical X=O group. Excellent $\Delta\nu/\nu$ plots against acetophenone were again obtained (Figure). These bands fell at 1199 cm.$^{-1}$ in the ethyl derivative and at 1200 in the n-butyl compound (in n-hexane) and they are clearly derived from the C=S group. The earlier assignments are therefore fully confirmed.

We have also examined the spectrum of methyl α-thionaphthoate in many solvents. This compound has a strong absorption at 1200 cm.$^{-1}$ which could well arise from the C=S link. However, neither this band nor any other in the vicinity showed any frequency change with alterations in the solvent. Indeed, the only bands which were at all sensitive were the δCH aromatic absorptions at 795 and 775 cm.$^{-1}$. These moved to higher frequencies on passing from dioxan to methylene iodide. This shift is in the opposite direction to that which would be expected from a C=S link but would be appropriate for deformation vibrations perturbed by association of the solvent with the ring. As will be seen, similar cases have been found with aromatic thio-ketones in which association seems to occur preferentially with the ring rather than with the C=S link. Presumably, the geometry of these compounds is such that the polarity of the C=S bond is much reduced so that the ring is actually the more polar. The method would not then be expected to yield a positive result for C=S links.

(b) *Thioamides.* Several workers have examined small groups of thioamides. Mecke

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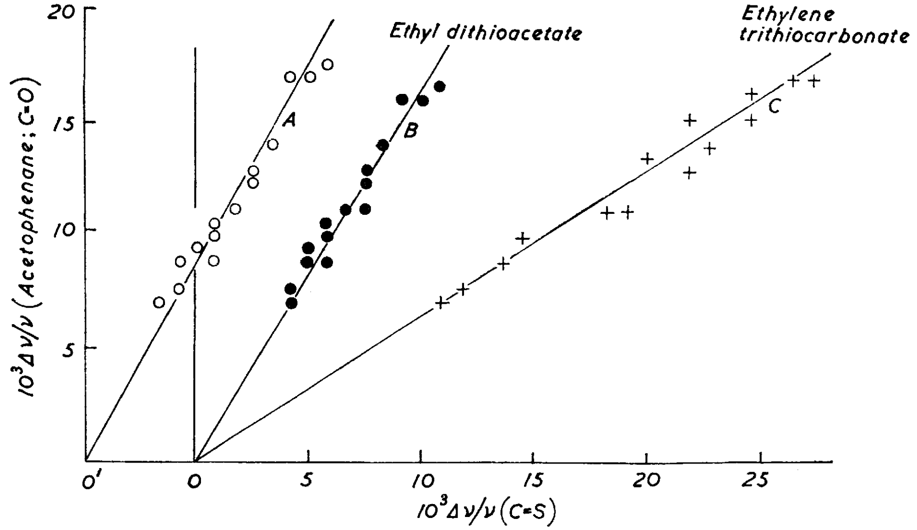
[8] Bak, Hansen-Nygaard, and Petersen, *Acta Chem. Scand.*, 1958, **12**, 1951.

[9] Mecke, Mecke, and Lüttringhaus, *Z. Naturforsch.*, 1955, **10**b, 367; *Chem. Ber.*, 1957, **90**, 975.

et al.[9,10] studied 13 such compounds and suggested an overall range of 1209—1040 cm.$^{-1}$ for the $>$C=S band. Marvel *et al.*[7] found a range of 1205—1130 cm.$^{-1}$ in four compounds, and Haszeldine *et al.*[3] 1430—1300 cm.$^{-1}$ in three others. Hadži [11] has made some detailed studies on acetanilides in which the characteristic absorption appears to be near 1000 cm.$^{-1}$. Individual assignments include alternative values of 1430 and 1300 cm.$^{-1}$ for the C=S of thioacetamide,[12,13] and a value of 830 cm.$^{-1}$ for the same band in dithio-oxamide.[14]

These compounds are therefore of particular interest in view of the wide differences found. Unfortunately, the solvent method is somewhat more limited in these cases than in that of the esters owing to difficulties in obtaining vapour-phase spectra and to insolubilities in non-polar solvents. It is not therefore possible to derive Δν/ν values based on vapour frequencies for comparison with carbonyl compounds. Nevertheless, some important indications can be obtained from the general pattern of solvent behaviour.

A, n-Butyl dithioacetate; B, ethyl dithioacetate; C, ethylene trithiocarbonate (1,3-*thiolan*-2-*thione*).



We have studied two thioamides in this way. These are tetramethylthiuram monosulphide and thioacetamide. The first of these behaves like the dithio-esters in showing only one band which is sensitive to the nature of the solvent. This occurs at 965 cm.$^{-1}$ in dioxan. As the nature of the solvent is changed towards proton-donating solvents such as bromoform and methylene iodide, this frequency falls systematically to lower values as shown in the table. The order of solvent effectiveness is exactly the same as that for carbonyl groups or for the C=S groups already identified.

Despite the absence of final confirmation from a Δν/ν plot it therefore seems highly likely that this is the C=S absorption. The spectral changes in thioacetamide with alterations of solvent are more complex, because this compound contains two different dipoles (NH_2 and C=S) which will react differently towards changes in their environment. Altogether, four bands appear to be solvent-sensitive. Three of these are at frequencies corresponding to NH stretching or deformation modes and are readily identified, because they behave in various solvents in precisely the way that would be expected. Thus, on passing from non-polar solvents to proton-acceptors the two NH stretching frequencies fall whilst the NH deformation mode rises. The remaining band is therefore that due to the other strongly polar group, the C=S link. The frequency is at 980 cm.$^{-1}$, close to the bands already assigned to other thio-amides, and the pattern of solvent behaviour is, as before, just that which would be expected from a group of this type.

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[10] Mecke and Mecke, *Chem. Ber.*, 1956, **89**, 343.
[11] Hadži, *J.*, 1957, 847.
[12] Mecke and Speisecke, *Chem. Ber.*, 1956, **89**, 1110.
[13] Davies and Jones, *J.*, 1958, 955.
[14] Scott and Wagner, *J. Chem. Phys.*, 1959, **30**, 465.

We would therefore assign the C=S link in these thio-amides to the 1000—950 cm.$^{-1}$ region, in agreement with Hadži.[11] However, this is not intended to define the overall range, as the ultimate frequency must be very dependent upon the degree of delocalisation of the π-electrons and so may well vary more widely.

One other compound of this type—to which the method proved inapplicable—was mercaptobenzothiazole. This compound is known to exist in the thioketo-form [15] but no solvent-sensitive bands in the 1000 cm.$^{-1}$ region could be found. The reasons for the failure of the method are different from those given for the methyl α-thionaphthoate. Mercaptobenzothiozole associates into a dimeric form in a way reminiscent of the carboxylic acids. Studies of the NH stretching bands at concentrations as low as 0·001M indicated that the compound was still largely associated. In such cases the solvent is unable to interact with the C=S link and no shifts occur. Similar results have been reported earlier for other strong intermolecular and intramolecular bonds.[16]

(c) *Thio-ketones.* Simple thio-ketones such as thioacetone polymerise into cyclic forms which lack the C=S link. Only in larger molecules does this bond retain its identity, and the compounds are then characterised by an intense blue colour. The most detailed study of thio-ketones is that made by Lozac'h and Guillouzo.[17] They compared the spectra of thiobenzophenone and ten of its substituted derivatives with those of the corresponding acetophenones. In each case the carbonyl band was replaced by a new band in the range 1207—1224 cm.$^{-1}$. No other systematic studies have been made although Bergmann [18] tentatively ascribed absorptions near 1300 cm.$^{-1}$ in thioxanthones and similar materials to the thioketo-group.

We have studied thiobenzophenone and 1-thiobenzoylnaphthalene. As in the case of the naphthyl ester already described, no significant frequency shifts occurred in any solvent, with the exception of changes in the out-of-plane aromatic deformation modes. These rose to higher frequencies in compounds in which association with the aromatic ring is likely. It therefore seems that the C=S link is again non-polar in these aromatic compounds. This is not unlikely if the size of the sulphur atom is such as to cause the C=S bond to lie out of the plane of the aromatic rings. In the absence of conjugation, the C=S bond would be effectively non-polar, as the electronegativity difference between carbon and sulphur is very small. This would also account for the fact that the thio-ketone absorption appears at a higher frequency than the C=S of thiocarbonyl chloride, as the frequency ultimately depends upon the degree of covalency of the bond.

DISCUSSION

The above results show that the method of solvent variation is very suitable for identification of group frequencies of polar links. It is not suitable for non-polar bonds. The revised assignments for C=S links now give the highest frequencies to thio-ketones followed by thio-esters which are greater than in thiocarbonyl chloride. Thio-amides show the lowest thiocarbonyl frequencies. This order of effectiveness of the substituents is significantly different from that of the carbonyl group and arises from the differences in polarity in the two cases. Carbonyl compounds are initially polar because of the electronegativity difference between the component atoms, and as a result of this the frequency is raised by inductive effects and lowered by mesomerism.[19] In the C=S link there is little or no initial polarity and it therefore resembles more closely the C=C links which fall in frequency under the influence of either induction or mesomerism. The highest C=C frequencies, apart from special cases of fluorinated systems, are those of fully covalent compounds such as but-2-ene, so that the high frequencies of the thiobenzophenones are not unreasonable. Substituents such as nitrogen atoms which can conjugate with the C=S link will increase its polarity and lower the frequency. This is consistent with the revised assignments for thio-amides. However, it must be stressed that the lowered frequency arises wholly from the polarity acquired in this way, so that in compounds in which this is inhibited the frequency would rise again to a value close to 1200 cm.$^{-1}$.

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[15] Flett, *J.*, 1953, 347.
[16] Bellamy and Hallam, *Trans. Faraday Soc.*, 1959, **55**, 220.
[17] Lozac'h and Guillouzo, *Bull. Soc. chim. France*, 1957, 1221.
[18] Bergmann, *J. Amer. Chem. Soc.*, 1955, **77**, 1549.
[19] Bellamy, *Spectrochim. Acta*, 1958, **13**, 60.