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SOME CONSIDERATIONS ON THE RAMAN BANDS OF O-ALKYL XANTHOGENATES IN THE 700-600 CM^{-1} REGION

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The Raman spectra of 11 kinds of O-alkyl xanthogenates in solutions and solid states were measured. The band patterns in the 700-600 cm^{-1} were examined in terms of the difference of phases, the behaviours on the change of solvents, and the intensities. From the results, origin of the characteristic band patterns was discussed.

In the present investigation, we have measured the Raman spectra of various O-alkyl xanthogenates (R-O-CSS$^-$) and, paying attention to the characteristic band patterns observed in the 700-600 cm^{-1} region, which seem to be related to the structures of R, the experimental results have been discussed in terms of the phases, the solvents and the intensities. At present, only two reports[1,2] on the Raman spectra of O-methyl xanthogenate can be found in literatures. The purpose of this note is to present the experimental facts which suggest the existence of rotational isomers in solutions for the samples with alkyl groups larger than methyl group.

The Raman spectra were measured with a JASCO Model J-800 Laser Raman Spectrophotometer, using the 488 nm line of an Ar ion laser as an excitation source. Since the samples in solutions were found to be unstable, when exposed to the laser beam irradiation, the rotational cell technique was used for the measurements for the solutions. The spectra for solid samples were measured by capillary method.

(1) The spectra for solids and solutions.

Table 1 The Raman bands of O-alkyl xanthogenates

Alkyl group	Solid state	Aqueous solution	
CH_3-	623(vs)	-	619(vs)
CH_3CH_2-	669(vs)	662(vs),	616(s)
$CH_3CH_2CH_2$-	662(vs)	662(vs),	618(s)
$(CH_3)_2CH$-	664(vs)	661(vs),	-
$CH_3(CH_2)_2CH_2$-	673(vs)	664(vs),	617(s)
$(CH_3)_2CHCH_2$-	667(vs)	666(vs),	618(s)
$CH_3CH_2(CH_3)CH$-	662(vs)	660(vs),	-
$(CH_3)_3C$-	654(vs)	656(vs),	-
$CH_3(CH_2)_3CH_2$-	664(vs)	665(vs),	618(s)
$(CH_3)_2CHCH_2CH_2$-	664(vs)	660(vs),	618(s)
$CH_3(CH_2)_2(CH_3)CH$-	662(vs)	659(vs)	-

In Table 1 are summarized the strong bands observed in the 700-600 cm^{-1} region. These bands may be attributed to the CS stretching vibrations[1,2]. It is noteworthy that in solid states, only one strong band is observed in all cases, while in the case of aqueous solutions, one or two strong bands are observed according to the types of R. The interesting fact is that when the carbon atom adjacent to the oxgen

Table 2 The behaviours of the bands according to solvents

Solvent	Ethyl-		n-Propyl-		iso-Propyl-
H_2O	662	616	661	617	660
0.05N KOH aq.	662	616	662(+1)	618(+1)	661(+1)
CH_3OH	664(+2)	618(+2)	663(+2)	620(+3)	663(+3)
Acetone	657(-5)	610(-6)	658(-3)	613(-4)	656(-4)

atom has no branching, two bands are observed in the CS stretching region, and that when there is the branching, the spectra exhibit only one band.

(2) The band behaviours due to the solvent effect.

In Table 2 are shown the effect of solvents on the wavenumbers of the bands in question. It is seen from this table that the behaviours of the two bands are similar for each of the types of R, and that the shifts are also similar in the magnitude and the direction for both of the cases of n-propyl and iso-propyl types. The former exhibits the two bands, and the latter, only one band.

Table 3 The relations for the intensities among the isomers

Alkyl group	Relative values of intensities
C_3-type	$(I_n^{662} + I_n^{618})/I_{iso}^{661} = 1.0$
C_4-type	$(I_n^{664} + I_n^{617})/I_{sec}^{660} = 1.2$
	$(I_{iso}^{666} + I_{iso}^{618})/I_{sec}^{660} = 1.1$

I_n^{660} denotes the intensities of the band at 660 cm^{-1} for n-type alkyl groups and the others have similar meanings.

(3) The scattering intensities.

Finally, we have examined these bands in view of their intensities. The integrated intensities have been measured relatively to that of the CS stretching vibration of thiocyanate ion. In Table 3 are shown the examples of the obtained ratios between the intensity sums for the samples having the two bands and the intensities for the corresponding isomers exhibiting the single band. It is seen from this table that the sums of the intensities for the n-propyl, n-butyl and iso-butyl types are approximately the same as the intensities of a single band of the corresponding isomers. These results can be most satisfactorily interpreted if we consider that in the case of appearance of the two bands, there exist two chemical species which give the Raman bands with similar scattering coefficients.

Within the limit of the experimental results so far described, they seem to suggest that the two bands observed for the solution samples come from the same vibrational mode. Furthermore, the results obtained here strongly indicate the possibility of the existence of rotational isomers, in which the carbon atom adjacent to the oxgen atom (C_α) plays an essential role. If the speculation is allowed by analogy with the cases of alkyl sulfides[3-5], it may be assumed that the higher frequency bands correspond to the trans conformations about C_α-O axis and the lower frequency bands, to the gauche ones. Further experimental and theoretical investigations are required now.

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