Infrared Spectra of Salicylaldehyde, Methylsalicylate and their Sodium Compounds

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Concerning the infrared spectra of conjugated chelate compounds, it is well known that the absorption bands associated with the OH stretching and the C=O stretching vibrations show some peculiarities that are not observed in the spectra of the usual hydrogen-bonded molecules.

The formation of the intramolecular hydrogen bond in conjugated chelate compounds may be mainly due to electrostatic and charge transfer forces. Though some interpretations of the spectra, common to various conjugated chelate compounds, have been given by considering resonance structures, a question as to what structure contributes predominantly to the resonance has not yet been solved completely. The important contribution of ionic structure to the resonance was pointed out by some investigators[1], based on the infrared studies of the C=O bands, while the ionic structure was disregarded by a few others[2] from the measurements of the OH bands. The OH band seems to be inappropriate for accurate measurement because of its broad band width. The intensity measurement of the C=O band has not yet been made. In these circumstances, more experimental knowledge is required to make an analysis of this problem. Salicylaldehyde and methylsalicylate are suitable for the intensity measurements of the C=O bands and for the present analysis.

The sodium compounds of salicylaldehyde and methylsalicylate are very interesting, because they are expected to have an intermediate character between salts and metal chelate compounds and further will be closely related to the hydrogen-bonded compounds. The measurements for these compounds, therefore, will not only make their structures clear but also give a valuable item of knowledge in regard to the hydrogen-bonded chelation.

Experimental

Measurements were made by a Perkin-Elmer Model 112 Infrared Spectrophotometer equipped with CaF_2 and NaCl prisms. For dilute solutions, fixed cells of 0.01, 0.05 and 1 cm. thicknesses were used, and the thicknesses of the thin cells were determined by the interference method. The slit widths for intensity measurements were kept constant and ranged from 0.07 to 0.15 mm. The integrated absorption intensity of a band, A ($mol^{-1}\cdot l.\cdot cm^{-2}$) was calculated by the following formula;

$$A=(K/Cl)\cdot\Delta\nu_{1/2}\cdot\ln(I_0/I)_{\max}$$

where C, l, $\Delta\nu_{1/2}$ and $\ln(I_0/I)_{\max}$ have their usual meanings and K is obtained from Ramsay's table[3], by use of the spectral slit width calculated by Kudo's equation[4].

The samples used were purified by distillation. The boiling points were as follows; 68.8~69.0°C/10 mmHg for salicylaldehyde, 73.0~73.5°C/5 mmHg for methylsalicylate and 51.0~51.2°C/9 mmHg for benzaldehyde. *o*-Methoxybenzaldehyde was prepared from salicylaldehyde and dimethylsulfate[5]. The boiling point was 37.3~38.0°C.

The sodium compounds of salicylaldehyde and methylsalicylate were prepared by mixing an excess of salicylaldehyde and methylsalicylate with ethylalcoholate[6]. The sodium compound of methylsalicylate was also prepared by throwing metallic sodium into methylsalicylate. Upon heating, the sodium compound of salicylaldehyde chared at ca. 250°C instead of melting and the sodium compound of methylsalicylate at ca. 180°C. From the titration with hydrochloric acid, it was determined that each compound contained two molecules of salicylaldehyde or methylsalicylate for a sodium ion.

Results and Discussion

The results for the C=O bands of salicylaldehyde and methylsalicylate in

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[1a] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

[1b] D. Hadzi and N. Sheppard, *Trans. Faraday Soc.*, **50**, 911 (1954).

[2a] M. Tsuboi, This Bulletin, **25**, 385 (1952).

[2b] M-L Josein, N. Fuson, J-M Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).

[2c] H. Tsubomura, ibid., **24**, 927 (1956).

[3] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

[4] K. Kudo, *J. Spectroscop. Soc. Japan* (*Bunkô Kenkyû*), **9**, 36 (1954).

[5] A. Kalschalowsky and St. v. Kostanecki, *Ber.*, **37**, 2347 (1904).

[6] N. V. Sidgwick and F. M. Bewer, *J. Chem. Soc.*, **127**, 2379 (1925).

TABLE I. THE C=O BANDS OF SALICYLALDEHYDE AND METHYLSALICYLATE IN CARBON TETRACHLORIDE

		ν_{max} cm^{-1}	Concn. $mol.\cdot l^{-1}$	$\ln(I_0/I)_{max}$	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ $mol^{-1}\cdot l.\cdot cm^{-2}$
Salicylaldehyde	I	1668	0.0942	2.487	7.00	2.60
	II	1668	0.0449	1.276	6.75	2.66
	III	1668	0.0634	1.814	6.80	2.70
	average	1668				2.65
Methylsalicylate		1683	0.0879	1.663	13.6	3.56

TABLE II. THE FREE C=O BANDS AND THE INTERMOLECULAR HYDROGEN-BONDED C=O BANDS OF BENZALDEHYDE AND *o*-METHOXYBENZALDEHYDE IN CARBON TETRACHLORIDE

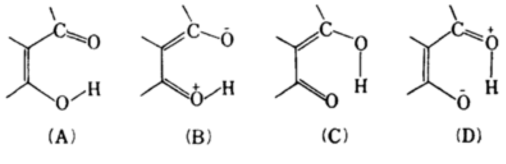
	ν_{max} cm^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ $mol^{-1}\cdot l.\cdot cm^{-2}$
Benzaldehyde	1708	8.40	2.36
Benzaldehyde+*n*-butanol	1707	15.4	2.96
o-Methoxybenzaldehyde	1694	8.2	2.60*
o-Methoxybenzaldehyde+*n*-butanol	1693	13.2	3.25*

* The intensities are summed up for two ν_{max} assigned to its two isomers, though the intensity of one of them, at 1667 cm^{-1}, is very weak.

carbon tetrachloride solution are tabulated in Table I. In order to know whether or not the intensity of the band alters with chelating, the spectrum of salicylaldehyde should be compared with that of *o*-methoxybenzaldehyde, as the effect of the conjugation with the benzene ring and that of the ortho-substituted oxygen atom on their C=O groups are the same for both compounds. The results of the measurements for *o*-methoxybenzaldehyde[7] are shown in Table II. Because the intensity of the C=O band for salicylaldehyde is nearly equal to that for *o*-methoxybenzaldehyde, it comes out that the chelation effect does not alter the intensity. As the intensity of the C=O band for methylsalicylate shows the normal value of esters[8], it appears that the chelation effect has a large shift for the C=O stretching frequency towards lower frequency region but hardly affects the intensity. The lack of intensity change may indicate that the change in the bond moment is inappreciable.

In Table II are given the results for the conjugated C=O groups forming the intermolecular hydrogen bond with *n*-butanol. Here, the volume percentages of *n*-butanol in carbon tetrachloride range from 30 to 50%. Almost all the C=O groups of the compound in these solutions form the intermolecular hydrogen bond, since the frequency at the maximum absorption and the intensity of the band do not change with the concentration of *n*-butanol. By the formation of the intermolecular hydrogen bond the intensity noticeably increases, while the change in the frequency is very slight. These phenomena are different from those observed in the chelate compounds and can be explained by Tsubomura's theory[2c].

For the conjugated chelate compounds the four possible resonance structures shown below should be taken into account.



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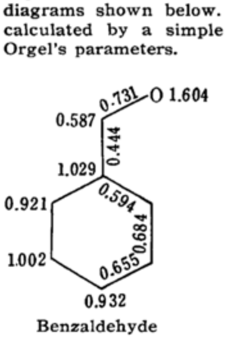
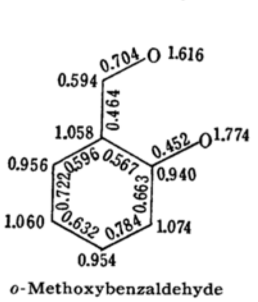
[7] The ortho-substitution effect can be estimated by the comparison between benzaldehyde and *o*-methoxybenzaldehyde. The decrease of the frequency and the increase of the intensity for the C=O band were observed by introducing the methoxy group. These changes are due to the migration of the lone pair electrons belonging to the oxygen atom and seem to be explained by the results expected from the molecular diagrams shown below. The molecular diagrams are calculated by a simple LCAO-MO method by use of Orgel's parameters.



Benzaldehyde



o-Methoxybenzaldehyde

[8] G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

TABLE III. SOLVENT EFFECT ON THE C=O BANDS OF SALICYLALDEHYDE AND METHYLSALICYLATE

	Solv.	ν_{max} cm^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol$^{-1}\cdot$l.$\cdot$cm^{-2}
Salicylaldehyde	chloroform	1666	9.3	2.60
	n-butanol	1667	8.8	2.52
	acetonitrile	1666	8.6	2.61
Methylsalicylate	chloroform	1678	19.8	4.16

TABLE IV. THE C=O BAND OF ENOL-FORM OF ACETYLACETONE IN CHLOROFORM

ν_{max} cm^{-1}	Concn. mol.$\cdot$l^{-1}	Enol* content %	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol$^{-1}\cdot$l.$\cdot$cm^{-2}
1615	0.103	78	62.8	9.15

* K. Kuratani, *Rept. Inst. Sci. and Technol., Univ. Tokyo*, **6**, 217 (1952).

By the formation of the chelate ring the C and D structures newly contribute to the resonance. The important contribution of the B structure was at first pointed out by Rasmussen et al.[1a)] and afterwards by Hadzi et al.[1b)] again, while the importance of the C structure was reported by Tsuboi[2a)], Josein et al.[2b)] and Tsubomura[2c)]. As it may be true that for a molecule having the carbonyl group the change in ionic character of C=O bond on chelate bonding contributes to the intensity increase of the C=O band, there seem to be two possibilities to account for the present results. First, if the C structure makes a significant contribution to the structure of the chelating compounds, the bond order of the C=O group will decrease and the appreciable change in the bond moment of the group will not occur, in accord with the results. Secondly, if both the structures of B and D equally contribute to the resonance, an increase in the contribution of the B structure will give rise to a decrease of the bond order and hence to the decrease of the C=O frequency, and the equal contribution of both the structures will not significantly alter the bond moment of the C=O group, because the directions of the polarities of both the resonance structures are opposite, and will result in the unaltered intensity of the C=O band. The second interpretation, however, seems to be less reasonable than the first, because in the second the D structure, in spite of its high energy, must contribute to the resonance to the same extent as the increase of the B structure.

In a molecule having a polar resonance structure the per cent contribution of each structure may vary with the change of solvent. As for such a molecule, a slight change in the per cent contribution gives rise to appreciable changes in the dipole moment and in the intensity of the infrared absorption band. The intensity of the C=O band for salicylaldehyde is the same in carbon tetrachloride, in chloroform and even in acetonitrile. This fact indicates the important contribution of non-ionic structures in this molecule. The chelation in methylsalicylate is not so strong as in salicylaldehyde because of the ester resonance[9)]. The contribution of the C structure to methylsalicylate, therefore, will be less important than the contribution to salicylaldehyde. In the case of methylsalicylate, the influence of polar solvent on the intensity of the C=O band was found.

As for β-diketones, conjugated chelate compounds take the enol forms. As the C=O bands of these compounds overlap with their C=C bands, the intensities of the bands appear to be very large. Rasmussen et al. described the fact that a very broad band, estimated to be more than a hundred times as strong as the normal carbonyl band, was observed in the range 1639~1538 cm^{-1}.

As is shown in Table IV, the integrated intensity of the broad band including the C=O and C=C bands measured for the enol form of acetylacetone is only about twice as strong as that of the usual conjugated aliphatic C=O band; e.g., the value for isophorone in chloroform is 4.6×10^4 mol$^{-1}\cdot$l.$\cdot$cm^{-2}. The interpretation for β-diketones will be essentially the same as that for salicylaldehyde. Since the normal value of the intensity of the C=O band for this molecule is expected, this fact indicates

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9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc., New York (1952), p. 164.

that the intensity of the C=C band increases by the chelation effect.

Concerning the band shapes for the chelate compounds, there can be found a relation between the C=O and the OH band. A compound having a sharp C=O band shows a broad OH band, and conversely a compound having a broad C=O band a sharp OH band. Strong chelation is accompanied by a sharp C=O and a broad OH band. Acetic acid is regarded as a sort of chelate compound. The C=O band measured in carbon tetrachloride solution is shown in Table VI. The association of acetic acid to the dimer is so strong that it dissociates with difficulty to the monomer even in 0.05 mol.$\cdot$l^{-1} concentration. It is interesting to notice that the intensity of the C=O band seems to be normal, though this band is assigned to the antisymmetric stretching vibration caused by the coupling of the two C=O groups.

TABLE V. THE C=O BAND OF ACETIC ACID DIMER IN CARBON TETRACHLORIDE

ν_{max} cm^{-1}	Concn. mol.$\cdot$l^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol$^{-1}\cdot$l.$\cdot$cm^{-2}
1713.5	0.0481	10.4	3.92

TABLE VI. THE BAND SHAPES OF C=O AND OH STRETCHING VIBRATIONS

	C=O band	OH band
Salicylaldehyde	sharp	broad
Methylsalicylate	broad	sharp
Acetic acid dimer	sharp	broad

TABLE VII. THE WAVE NUMBERS FOR SALICYLALDEHYDE, METHYLSALICYLATE (IN LIQUID) AND THEIR SODIUM COMPOUNDS (IN NUJOL)

Salicylaldehyde	Sodium compound of salicylaldehyde	Methylsalicylate	Sodium compound of methylsalicylate
		701 w	701 w
715 m	731 m		712 m
766 s	766 s	759 s	758 m
	777 m		771 m
		800 m	801 w
		813 sh	806 w
		848 m	850 w
883 s	893 s	866 m	860 sh
		963 m	964 m
1023 m	1036 m	1032 m	1032 m
		1090 m	1085 m
1113 m	1119 s	1136 m	1148 sh
1149 m	1148 s	1158 m	1157 m
1182 s	1180 s	1195 m	1190 m
1201 sh			
1227 s	1246 s	1212 s	1213 s
1276 s	1279 m	1253 m	1257 m
		1301 s	1306 sh
1319 m	1315 m	1325 s	1316 s
		1439 s	1439 s
1577 w		1587 m	1540 m
1619 m	1600 m	1615 m	1607 w
1663 s	1680 s	1679 s	1682 s
3100 w	3344 m	3141 m	3206 m
			3351 m

The wave numbers of the infrared bands for the sodium compounds of salicylaldehyde and methylsalicylate observed in the solid state are tabulated in Table VII, together with the wave numbers for salicylaldehyde and methylsalicylate in the liquid state.

From the infrared measurements and the titration of sodium ion, it can be seen that a sodium ion links to two salicylaldehyde molecules, one of them being a molecular rest ion of salicylaldehyde and the other a salicylaldehyde molecule. The structures of these compounds will be illustrated in Fig. 1.

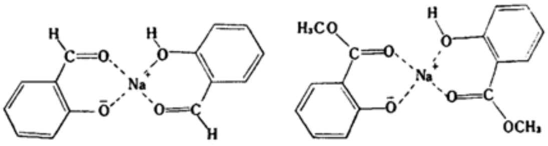

Fig. 1. The sodium compounds of salicylaldehyde and methylsalicylate.

The OH stretching vibrations of the sodium compounds show higher frequencies than those of salicylaldehyde and methylsalicylate. The broad band at 3100 cm^{-1} for salicylaldehyde changes into the sharp band at 3344 cm^{-1} for the sodium compound. The band at 3141 cm^{-1} for methylsalicylate separates into the two bands having their maxima at 3351 cm^{-1} and 3206 cm^{-1} for the sodium compound. The shifts of the OH stretching vibrations caused by changing salicylaldehyde and methylsalicylate into their sodium compounds indicate that the strong intramolecular hydrogen bond in the former varies into the intermolecular hydrogen bond in the latter. The two OH bands for the sodium compound of methylsalicylate may show the existence of the two different types of intermolecular hydrogen bond.

Concerning the sodium compounds, only one band can be assigned to the C=O stretching vibration for each compound. With the vibrations of metal chelate compounds, the couplings between ligand molecules are usually neglected. This approximation may be applied to these sodium compounds because of the weakness of the metal-oxygen coordinate bonds. The same C=O stretching frequencies for salicylaldehyde and its molecular rest, coordinating to a sodium ion, suggest that the two carbonyl bonds are in the same electronic state. It is deduced that the lone pair electrons on the ionized oxygen in the molecular rest delocalize too little to influence the carbonyl group through the benzene ring. The fact that the carbonyl frequency of the C=O band for sodium compound of salicylaldehyde is higher than that for salicylaldehyde, may be explained by the small value of the electron affinity of sodium ion. As for the electron transfer of the oxygen atom in the carbonyl group, the larger the electron affinity of electron acceptors, the easier the electron transfer. The lone pair electrons on the oxygen atom, therefore, are less drawn by sodium ion than by proton and the frequency of the C=O band is higher for the sodium compound than for salicylaldehyde. The frequency of the C=O band for the sodium compound of methylsalicylate is slightly higher than that for methylsalicylate[10]. Since the coordinate bond between the sodium ion and the carbonyl group is very weak, the carbonyl group of the sodium compound of salicylaldehyde as well as that of *o*-methoxybenzaldehyde will be rather akin to that of virtual non-chelate salicylaldehyde. The difference in the C=O frequency between salicylaldehyde and its sodium compund is 17 cm^{-1}, while that between methylsalicylate and its sodium compound is only 3 cm^{-1}. This fact indicates the strong chelation in salicylaldehyde. This agrees with the results obtained by the solvent effect and the band shapes. The configuration of the sodium compound is probably of a tetrahedral type, since the available orbitals of sodium ion to form the coordinate bond are sp^3 hybrid. However, it has recently been reported[11] that the sodium compound of salicylaldehyde does not form any chelate ring because of the observed high frequency of the C=O band. Based on the present studies this opinion can be left out of consideration.

As regards chelate compounds, the bands assigned to the phenolic C–O stretching vibrations are of considerable interest, because no definite assignment for these bands has yet been made. By comparing the absorption spectrum of salicylaldehyde or methylsalicylate with that of its sodium compound respectively, the phenolic C–O bands are reasonably assigned. The results obtained are listed in Table VIII. The relations between wave numbers of C=O stretching and those of phenolic C–O stretching vibrations are given in Fig. 2.

TABLE VIII. THE WAVE NUMBERS OF C=O AND PHENOLIC C-O STRETCHING VIBRATIONS

	Salicylaldehyde		Methylsalicylate	
	C=O	C-O	C=O	C-O
Na$^+$	1680	1246	1682	1213
H	1663	1276	1679	1212
Ti^{4+}	1637	1313	1651	1246
Cu^{2+}	1612	1340		

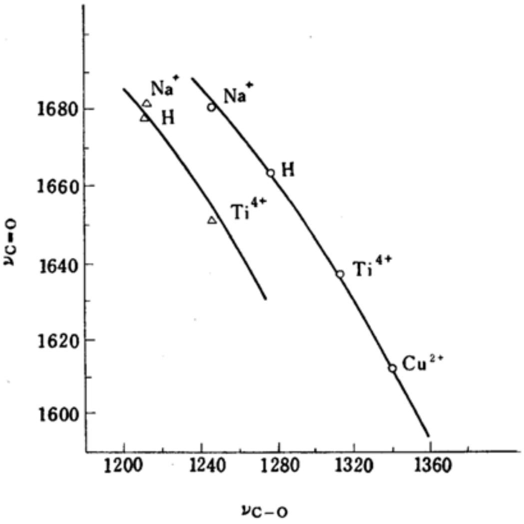

Fig. 2. The relations between the wave numbers of C=O stretching and those of phenolic C-O stretching vibrations. ○ Salicylaldehyde and its metal complexes. △ Methylsalicylate and its metal complexes.

In Table VIII and Fig. 2, copper complex and titanium complexes[12] are shown together. The larger the wave number of C=O stretching vibration, the smaller the wave number of C–O stretching vibration. The reason for this may be as follows. In these chelate compounds, as the double bond character of the C=O bond decreases by the electron migration from the carbon to the oxygen, the electron migration from the oxygen to the benzene ring and the

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[10] It is supposed that the C=O frequency of the sodium compound of methylsalicylate is hardly affected by the change in the nature of the C–O bond neighboring the C=O bond.

[11] P. Chiorboli and P. Mirone, *Ann. chim.*, **48**, 363 (1958).

[12] A. Yamamoto, to be published.

double bond character of the C–O bond increase. These relations are nearly linear and the curve for salicylaldehyde and its complexes and that for methylsalicylate and its complexes are parallel. From Fig. 2, it follows that the electron affinities of these electron acceptors are probably in the order of $Cu^{2+} > Ti^{4+} > H > Na^{+}$.

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