

AN INFRARED STUDY OF THE ADSORPTION OF CARBON DIOXIDE ON TIN

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Abstract. The interaction of carbon dioxide with tin has been investigated spectrophotometrically. Evidence has been found for physisorption and chemisorption of carbon dioxide on tin together with partial dissociation of carbon dioxide molecules into carbon monoxide and oxygen. This is accompanied by the successive formation of two different types of carboxylates ($1580, 1405 \text{ cm}^{-1}$) and (1815 cm^{-1}) which is assigned to carboxylate, linear type (polar adsorption of carbon dioxide), or to the dissociative adsorption of carbon dioxide; oxide ($650, 418 \text{ cm}^{-1}$); bridged (1840 cm^{-1}), linear (i.e. II-bonded to tin) carbonyl (1895 cm^{-1}); and terminal carbonyl (2050 cm^{-1}). An increase of time of contact of carbon dioxide gas with tin sample to two hr led to the disappearance of the 1815 cm^{-1} band with the simultaneous appearance of $1645, 1470,$ and 1240 cm^{-1} bands in addition to the 3620 cm^{-1} band characteristic of a bicarbonate species. Heating the sample at a temperature of 150° in carbon dioxide for three hours led to the disappearance of the previously mentioned species and the appearance of absorption bands characteristic of a bridged carbonate species ($1810, 1195, 785 \text{ cm}^{-1}$). The relationship between these different species has been explained.

Introduction

The adsorption of carbon dioxide on metal and metal oxides such as alumina has been studied by infrared spectrometry.¹⁻³ Other oxide systems such as titania,⁴ magnesium oxide,⁵ beryllium oxide,⁶ as well as alkali halides⁷ have been shown by infrared studies to adsorb carbon dioxide. No data is available about the feasibility and amenability of adsorption of carbon dioxide on tin although it is an interesting surface in that it can be oxidized to SnO, which shows both acidic and basic properties.^{8,9} Consequently, carbon dioxide should be very strongly adsorbed on it. Therefore, in this paper an attempt was made to study the adsorption of carbon dioxide on tin as a function of time and temperature.

Experimental Techniques

Of the six standard grades of tin, the chempure tin powder which is 99.997% pure was used for studies of adsorption of carbon dioxide. Because of the need to obtain suitably intense spectra high area samples are needed. These are usually in the form of powders to increase the available surface for adsorption and to decrease the particle size below the wave length of the infrared radiation, so as to minimize the scattering losses. Therefore, of the three finenesses, namely: 100, 200, 300 mesh, the 300 mesh size was used. Microscopic, infrared and atomic

absorption analysis of the tin powder showed that it is highly pure and free from impurities. In order to determine that the surface is still clean when adsorption occurs elemental chemical analysis of classical methods and atomic absorption method were conducted. Moreover, it is well established¹⁰ that one of the truly great advantages of the infrared method of chemical analysis is that it can be applied to virtually all materials, almost regardless of phase or phase mixtures, colloidal state, turbidity, molecular weight, solubility, "blackness," and nearly every other gross chemical or physical property. With proper (and usually simple) techniques, nearly any material can be prepared so that its infrared spectrum can be obtained. The technique used in this paper is that of unsupported metal samples described in the literature.^{10,11} One gram of chempure tin -300 mesh powder was transferred into a clean and a dry pyrex flask filled with carbon dioxide gas. Replacement of air in the pyrex flask by carbon dioxide was easily achieved owing to the fact that the specific gravity of carbon dioxide is relatively much greater than that of any other air-constituent gases, *viz*, the specific gravity of CO₂, N₂, O₂ : 1.53, 0.96, 1.10, respectively (air = 1). Consequently, no vacuum was maintained, especially we investigated the mechanism of adsorption and reaction of carbon dioxide with tin as a function of time and temperature and not as a function of pressure. The infrared spectra of the sample were obtained by means of UR-10 and Beckman IR-20 spectrometers according to Stimson and O'Donnel procedure described in detail in the literature.^{10,11} It is worthy to mention

that it is well established that in contrast to the adsorption of carbon monoxide that of carbon dioxide was fairly reproducible and was not dependent on the method of treatment the sample. Since tin is stable in moist air at temperature below 200°C , the role of moisture, which is usually present in air, on adsorption of carbon dioxide on tin powder was investigated by carrying the experiments with moist carbon dioxide obtained by the reaction of pure HCl with pure K_2CO_3 without drying it by passing through conc. H_2SO_4 .

Results and Discussion

The results of infrared spectrometric investigation and the corresponding spectra of the adsorption of carbon dioxide on tin are shown in Figs. 1-4 and Reaction Schemes 1-2. The assignment of structures for the adsorbed species, has been made by using information derived from spectrometric studies of metal carbonyls.¹²⁻¹⁴ The assignment of bands is simplified by their time and temperature dependence. Thus, when carbon dioxide was admitted to tin particles for 5 min absorption bands appeared at 1580 and 1405 cm^{-1} which are assigned to the asymmetric and symmetric stretching vibrations of the two carbon oxygen bonds^{11,15} (Fig. 1). If the time of treatment of tin sample with carbon dioxide is increased to 30 min the infrared spectrum shown in Fig. 2 is obtained. The vibration frequency at 1840 cm^{-1} seems to be due to a bridged carbonyl species bond to a surface tin atoms by covalent bonds as shown by structure II. The metal-carbon bonds are formed by contribution of electrons from both the adsorbent and the adsorbate. On the other hand, the absorption band at 1895 cm^{-1} arises from the dissociative adsorption of carbon dioxide on edge and/or corner tin atoms possessing relatively greater valence-electrons than tin atoms in planar positions. Binding electrons are supplied by carbon and tin atoms. It is to be noted that although this species absorbs below 2000 cm^{-1} it is more likely a linear rather than a bridged carbonyl as some investigators suggest,¹⁶ because the bridged structure should produce two absorption bands, due to the asymmetric and symmetric metal-carbon stretching vibrations.^{17,18} The relatively high absorption band at 2050 cm^{-1} seems to be due to a terminal carbonyl (structure IV). Both binding electrons are considered to be supplied by carbon monoxide. This may be understood if we take into consideration that it is well established that carbon dioxide dissociates on adsorption to carbon monoxide which forms the carbonyls and oxygen,¹⁹⁻²² which is adsorbed on to free tin sites. The appearance of absorption bands at 2050 , 1895 and 1840 cm^{-1} (Fig. 2) may be ascribed to either the heterogeneity of the surface, with some sites being more active than others²³ or to the repulsive interaction between

adsorbed molecules.²⁴ Indeed, infrared evidence for surface heterogeneity has been obtained in many instances. The adsorption of a compound may give rise to several absorption bands which correspond to independent surface species, each held to a particular type of surface site. Variations have been found in the frequencies and intensities of bands of adsorbed substances as the coverage of the surface was increased. The assignment of the band 1895 cm^{-1} (structure III) to a linear and not to a bridged structure is in agreement with the theory of Blyholder.^{17,18} It was postulated by the latter worker that increased participation of metal valence-electrons is needed to produce the low frequency ($\sim 2000\text{ cm}^{-1}$) carbonyl bands for adsorbed carbon monoxide. As a result the carbon-tin bond strength is increased and the carbon-oxygen bond was decreased, the metal valence-electrons enter a II-antibonding orbital for carbon monoxide (structure III). The absence of oxygen assists the employment of metal valence-electrons of edge and corner sites for bonding the carbon monoxide molecules and a lower carbonyl frequency would ensure (structure III). It is also equally possible that adsorption of carbon dioxide on these metal sites gives low frequency carboxylate species (1580 , 1405 cm^{-1} , Fig. 1). However, the released oxygen from the partial dissociation of carbon dioxide molecules is adsorbed on edge and corner tin atoms from which it attracts some of their valence-electrons and inhibits the formation of II-bonding between these tin atoms and carbon of carbonyl groups. This decreases the strength of tin-carbon monoxide bond and displaces its (carbonyl) band to higher frequency, namely 2050 cm^{-1} (structure IV, Fig. 2). The same is true for carboxylate species (structure I), which is formed as a result of adsorption of carbon dioxide on edge and corner tin atoms before attracting from them some of their valence-electrons by oxygen as it occurs in the formation of the carboxyl species represented by structure VII a, Fig. 2. The partial dissociation of carbon dioxide molecules into carbon monoxide and oxygen has been confirmed by spectroscopic analysis¹⁹ and is consistent with the appearance of broad absorption bands of medium intensity at 650 , 418 cm^{-1} characteristics of metal oxide, namely $\text{Sn}=\text{O}$,^{11,15} (Fig. 2). This lends support from the appearance of absorption bands at 3620 cm^{-1} characteristic of stretching frequency of hydroxyl group.^{10,11,15} Indeed, it has been established²⁵ that the surfaces of all oxides are hydroxylated through their interaction with atmospheric water. These surface hydroxyl groups play a fundamental role in the adsorption of molecules, with which they interact by a process of hydrogen-bonding. Infrared spectroscopy is of greatest value in observing this perturbation of the surface groups which occurs during the adsorption.

The absorption band at 2195 cm^{-1} (structure V,

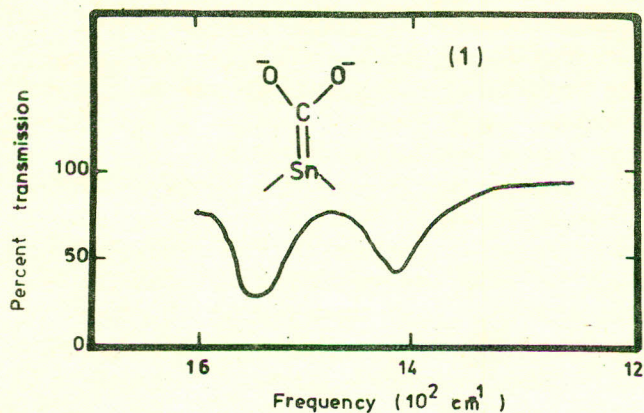


Fig. 1. Infrared spectra of tin after treatment with carbon dioxide for 5 minutes.

N.B. This spectrum was obtained with moist as well as with dry carbon dioxide.

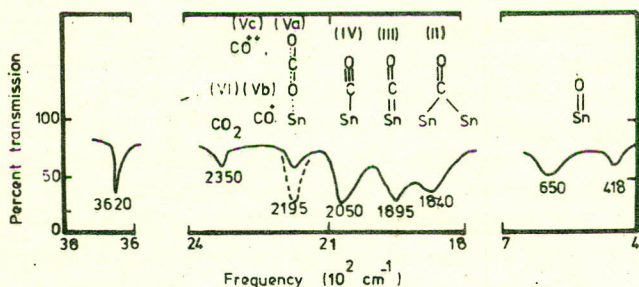


Fig. 2. Infrared spectra of tin after treatment with moist carbon dioxide for 30 minutes.

N.B. The band 2195 cm^{-1} (dotted) was obtained after heating the sample with excess CO_2 for 60 minutes. If the CO_2 was dried before interaction with tin the 3620 band disappeared (i.e. not appeared).

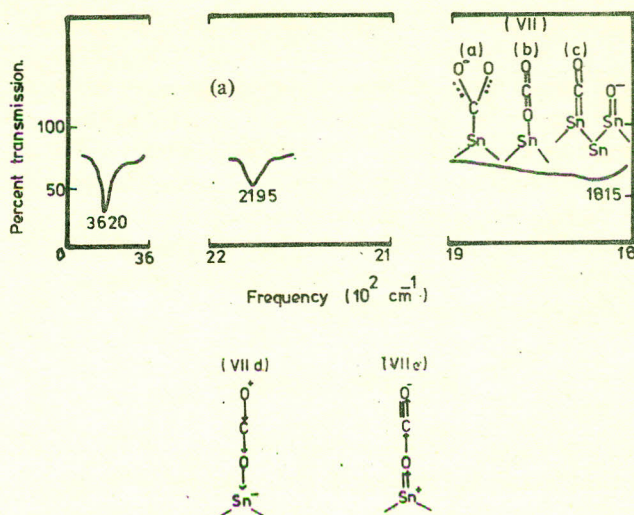
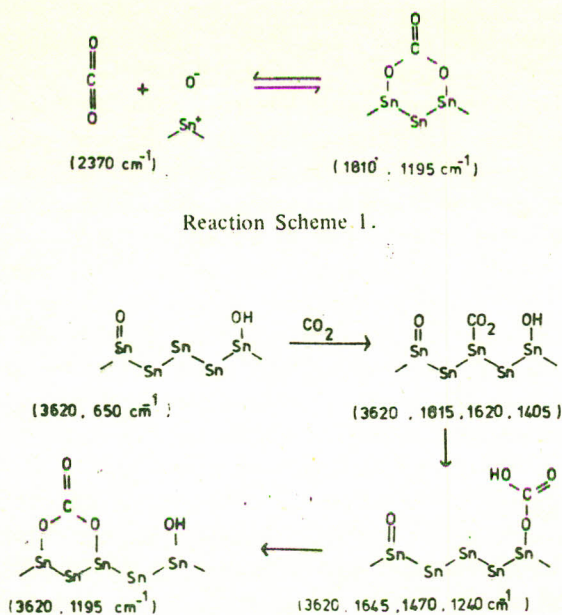


Fig. 3. Infrared spectra of carbon dioxide chemisorbed on tin; time of treatment with carbon dioxide: (a) one hour, (b) two hours.

N.B. In case of (a) the band 3620 cm^{-1} was obtained if moist CO_2 was used. If dry CO_2 was used no absorption at 3620 cm^{-1} was observed. In case of (b) all the spectrum was obtained only with moist CO_2 . If dry CO_2 was used a spectrum similar to 3 (a) was obtained.

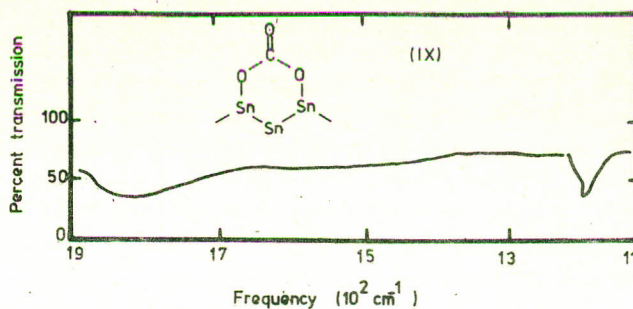


Fig. 4. Infrared spectra of tin after heating with moist carbon dioxide for three hours.

N.B. If dry CO_2 was used a spectrum similar to 3(a) was obtained.

Fig. 2) lies above that for gaseous carbon monoxide (2143 cm^{-1}), whereas all metal carbonyls with linear structures (structures No. III and IV, Fig. 2) absorb below this frequency.¹²⁻¹⁴ Carbon dioxide absorbs at 2350 cm^{-1} in the gas phase (structure VI, Fig. 2). This

band may be ascribed to the asymmetric stretching vibration of a species represented by the structure V a, Fig. 2, which has essentially the structure of carbon dioxide. However, this assignment is rejected by the absence of the symmetric stretching vibration. If we assumed that the symmetrical vibration produced a band of undetectably low intensity, this would indicate the metal-oxygen bond is extremely weak and that this structure O-C-O behaves like the carbon dioxide molecule in which the symmetric stretching band is forbidden in the infrared spectrum for symmetrical reasons.²⁶ This band may be assigned to CO species adsorbed to the surface by dipolar forces but the rather larger displacement of 59 cm^{-1} to higher frequency is difficult to reconcile with that explanation. The shift is in the direction opposite to that normally produced by polar environments.²⁷ No satisfactory explanation was found, however, for the high frequency of the observed band. The intensity of this band increased five-fold when the sample was heated for 60 min to 150° in contact with excess gaseous carbon dioxide. The proximity of the band frequency to that of gaseous carbon monoxide is consistent with the structure of the adsorbed species which still retains the essential triple-bond character for the carbon-oxygen bond.

An alternative explanation has been suggested for the origin of the high frequency bands in the spectrum of adsorbed carbon dioxide. The species responsible for the bands were considered to be partially or completely ionized.^{20,28} It seems that the positive ion CO^+ acts as the surface species (structure V b Fig. 2) responsible for the increased frequency from 2143 to 2195 cm^{-1} . Indeed, it has been reported that the removal of an electron from the carbon monoxide molecule strengthens the carbon-oxygen bond and results in an increased force constant and vibrational frequency and a decreased internuclear distance. The spectroscopic parameters given by Herzberg²⁹ give vibration frequencies of (CO) and (CO^+) to be 2143 and 2184 cm^{-1} , respectively. While this explanation would adequately account for bands at frequencies between those of gaseous (CO) and gaseous (CO^+) , some additional explanation is needed for absorption band frequencies greater than 2184 cm^{-1} . The removal of a second electron from carbon monoxide has been suggested by some investigators³⁰ to account for higher frequency than 2184 cm^{-1} resulting from adsorption of carbon monoxide. This, they believed, would cause a further strengthening of the carbon-oxygen bond and a subsequent increase of frequency. A value of 2205 cm^{-1} has been calculated for (CO^{++}) species (structure V c, Fig. 2). Some investigators have correlated the vibration of carbon monoxide in various environments, of valence-electronics in the molecule. A hyperbolic relationship was assumed to exist between the vibration

frequency and the number of valence-electrons for the species (CO) and (CO^+) , i.e. $\text{CO} = 2143\text{ cm}^{-1}$, ten valence-electrons; $\text{CO}^+ = 2184\text{ cm}^{-1}$, nine valence-electrons. It was further postulated that the vibrational frequency of the ion CO^- was 0.0 cm^{-1} , and that this hypothetical species with twelve valence-electrons, provided a further point for the construction of the hyperbola. When experimental values for carbonyl frequencies of adsorbed carbon monoxide were fitted to the hyperbolic curve, fractional values were indicated for the number of valence-electrons in the surface species. These fractions were believed to be characteristic for the individual metal substrates. Accordingly, the characteristic fractions and the vibration frequencies of the adsorbates and products are related to the catalytic activities of the metals.

A difficulty inherent in the consideration of ionized species CO^+ is the relatively large spectral frequency shifts which account for the formation of such weak adsorbent-adsorbate bonding. Moreover, the species (CO^+) and (CO^{++}) have been postulated without regard for the electron donor-acceptor properties of the adsorbent.

Since the carbon-oxygen stretching band for borane carbonyl ($\text{H}_3\text{B}:\text{CO}$) occurs at 2164 cm^{-1} ,³¹ that is above the frequency of gaseous carbon monoxide, consideration would be given to the possibility that the adsorbed carbon monoxide frequency above 2140 cm^{-1} belong to species bound to the surface merely by a σ -bond involving the lone-pair electrons of the carbon atom. Bands between $2140\text{-}2160\text{ cm}^{-1}$ might be explained in this way, although it can't be stated directly that frequencies as high as 2200 cm^{-1} can arise from such bonding. Frequencies above 2164 cm^{-1} must require surface sites which are more electron deficient than BH_3 , if the carbonyl frequency is taken as an index of the electron acceptor capacity of the atom to which the carbon monoxide is coordinated.

The assignment of the absorption band at 2350 cm^{-1} to gaseous carbon dioxide which is physically adsorbed is more straight forward as it falls well within the usual limits for this mode of vibration.^{11,15}

Referring to Fig. 3 it has been reported that absorption in the 1800 cm^{-1} (1815) region could be accounted for by an equilibrium of the type shown in the reaction scheme No. 1.³² Associating this bridged structure with 1815 cm^{-1} band is inherently unlikely because it is well established¹² that the bridged structure is associated with 1850 cm^{-1} band with its corresponding symmetrical stretching vibration at 1180 cm^{-1} alone. This band is the only one that showed a progressive decrease in intensity with time. No other bands in the whole of the observable region ($4000\text{-}1000\text{ cm}^{-1}$) showed parallel behaviour. Moreover, absorption in this region for inorganic C-O bonds is not very common.³³ According to the available

data^{12,33} this band may be assigned to three types of structures which are very simple and symmetrical which meet the requirements of the existence of only one infrared active band of this type. One structure being a carboxylate (structure VII a, Fig. 3). The second structure is the linear one (structure VII b). The third structure is that corresponding to dissociative adsorption of carbon dioxide (structure VIIc). This last possibility satisfies the infrared requirements^{12,33} and is quite likely for the existence of three vacant cationic sites in close proximity in sufficient concentrations to give the bands of such observed intensity.

It is to be noted that we have assigned the absorption band at 2195 cm^{-1} to the linear form (structure VI, Fig. 2). The C—O bond (dotted line) in $\text{Sn}-\text{O}^-\dots\text{C}^+ \equiv \text{O}^-$ was very weak and the corresponding stretching frequency fell outside the range of observation (1000 cm^{-1}). Alternative ways of writing the linear structure (VII d and e) are taken into consideration. The carboxylate structure (VII a) is quite likely because of the implication of electron transfer from a tin cation which has nearly no affinity for electrons, whereas carbon dioxide has a relatively high electron affinity (3.8 eV),³⁴ to the adsorbed molecule. Furthermore, carboxylate groups have infrared active bands corresponding to the asymmetric and symmetric C—O stretching frequency in the region under investigation,^{35,36} and both were observed at 1620 and 1405 cm^{-1} . The assignment of these bands to the carboxylate species raises the problem of whether there are also carbonate groups on the surface. Un-coordinated free carbonate ions of D_{3h} symmetry have only one active mode in the region above 1000 cm^{-1} ,³³ viz., at $1450 \pm 40\text{ cm}^{-1}$. Monocoordination splits this frequency to 1470 ± 20 and $1365 \pm 5\text{ cm}^{-1}$ and dicoordination to $1610 \pm 20\text{ cm}^{-1}$ and $1270 \pm 10\text{ cm}^{-1}$. As no bands with the exception of 1620 and 1405 cm^{-1} which cannot be accounted for the bicarbonate ion, in any of these positions are found in the spectrum of carbon dioxide on tin, uni- and bi-dentate carbonate species are ruled out. The question remains whether the bicarbonate species contributes to the intensity of the bands 1620 and 1405 cm^{-1} . This problem was resolved by attempting to assign other bands in Fig. 3. The other bands, namely 3620 , 1645 , 1240 cm^{-1} are believed to be those of a bicarbonate species. The key to this assignment is the band at 3620 cm^{-1} . The frequency indicates that it is likely to be an all stretching vibration. The assignment of the 3620 cm^{-1} band to ν_{OH} for OH monomeric bicarbonate group, in agreement with the data available in the literature^{11,37}, is straightforward; the assignment of the other peaks at 1645 , 1470 and 1240 cm^{-1} which appear simultaneously, is more difficult. The spectra of monomeric bicarbonate obtained recently by heating crystalline

(dimeric) potassium bicarbonate³⁸ are given in Table. 1.

The higher frequency 3620 cm^{-1} compared with 3390 cm^{-1} observed for the adsorbed bicarbonate ion compared with the monomeric ion in a potassium bromide matrix suggests that the former is completely non-hydrogen bonded and undergoes no interaction at all with the surface OH groups. The assignment is further supported by the absence of surface of tin hydroxy group of the highest frequency, namely $3800\text{--}3770\text{ cm}^{-1}$ at the same time that the bicarbonate group at 3620 appears. On Peri's classification³⁷ of the type of hydroxy groups, the highest frequencies $3800\text{--}3770\text{ cm}^{-1}$ correspond to a vibration of a hydroxy group surrounded by four oxide ions and completely isolated from all others. However, Dunken and Fink³⁹ have postulated the opposite, that they correspond to an OH group surrounded by four cations. The agreement of the observed frequencies of adsorbed carbon dioxide with those of monomeric bicarbonate ion would be entirely satisfactory with the exception of the absorption band at 1338 cm^{-1} . It seems likely that the strong band observed at 1470 cm^{-1} is due to the HCO_3^- group. It is very far removed from the expected absorption region of the missing symmetrical frequency ($1380\text{--}1300\text{ cm}^{-1}$), although Lindquist and Rea³ in their study of the carbon dioxide—alumina system similarly did not observe any bands in $1400\text{--}1300\text{ cm}^{-1}$ region. The band at 1470 cm^{-1} , if it is due to the bicarbonate group, must be the other wise missing symmetrical stretching frequency. Its intensity is about 1.5 times that of the 1645 cm^{-1} band which is approximately the same ratio as in the monomeric HCO_3^- ion. The crystalline alkali metal bicarbonate, which are strongly hydrogen bonded dimers⁴⁰ have symmetrical stretching vibration which are very broad and vary between $1300\text{--}1410\text{ cm}^{-1}$,⁴¹. The symmetrical stretching frequency remains fairly constant at around $1630 \pm 20\text{ cm}^{-1}$. Moreover, sodium ethyl carbonate ($\text{C}_2\text{H}_5\text{—O—CO}_2\text{Na}$), in which the hydrogen of the bicarbonate group has been replaced by the ethyl group, thus removing the possibility of hydrogen-bonding, has asymmetric vibration at 1164 vs cm^{-1} and symmetric stretching at 1437 cm^{-1} . Accordingly, it may be safely stated that there are no rules governing the position of the CO_3^{2-} symmetrical stretching in bicarbonate and, although 1470 cm^{-1} is rather outside the usual limit, it is not out of question to assign it to the symmetrical stretching frequency of a surface monomeric bicarbonate group. Further evidence for this assignment is produced by considering the intensity ratio of the $1645\text{--}1470\text{ cm}^{-1}$ bands. The assignment of 1645 cm^{-1} band to the asymmetric stretching frequency of HCO_3^- group is more straightforward as it falls well within the usual limits for this mode of vibration. The 1240 cm^{-1}

band, as a consequence is the C—O—H bending mode (1211 for HCO_3^-), Table 1.

The assignment of 1470 cm^{-1} band to the bicarbonate ion raises, also, the problem of whether there are also carbonate groups on the surface contributing to the appearance of this band. This has been established by varying the time of contact of the tin sample with carbon dioxide and observing the changes in the intensities of the various bands. If the bands 1670, 1645, 1620, 1470, 1405 and 1240 cm^{-1} are all vibration modes of the same surface species (bicarbonate) then plotting the intensity of any one band against that of any other should give a straight line passing through the origin. Any deviation from the linearity, or failure of any line to pass through the origin, would suggest a contribution to one of the bands from some other species, e.g. carbonate ion, assuming, of course, that the adsorption behaviour of the two species is different. The method also breaks down if there is an equilibrium: $\text{carboxylate} \rightleftharpoons \text{bicarbonate} \rightleftharpoons \text{carbonate}$. Fig. 5 shows the relative peak intensities plots of all bands against the 1645 cm^{-1} band. The intensity of the plots is sufficiently good to justify the assignment of the 3620, 1645 and 1470 cm^{-1} bands to the same species, namely the bicarbonate. The band at 1240 cm^{-1} , however, gave very poor agreement with the others, and only the previous strong arguments for assigning it to the C—O—H bending mode lead us to suppose that it was at all associated with the other bicarbonate ion frequencies. The good proportionality between the 1645 and 1470 cm^{-1} bands, and the fact that the line passes through the origin, would tend to rule out any appreciable contribution of carbonate ion to the intensity of the latter band. It also confirms the assignment of the 1470 cm^{-1} band as the symmetrical stretching frequency of the adsorbed bicarbonate group. On the other hand, the bands at 1620 and 1405 cm^{-1} gave disagreement with the others indicating that they are not at all associated with the bicarbonate ion frequencies. The absence of proportionality between the 1620, 1405 cm^{-1} bands and the other

TABLE 1. INFRARED SPECTRA OF TIN AFTER TREATMENT WITH CARBON DIOXIDE FOR 5 MINUTES.

Frequency (cm^{-1})	Assignment	References
1580 vs	Asymmetric stretching vibration of carboxylate.	11, 15
1405 s	Symmetric stretching frequency of carboxylate.	11, 15
528 ms	Sn-C stretching vibration.	32
420 m	Sn-C deformation vibration.	32

s : strong; m : medium; w : weak; v : very; b : broad; sp : sharp.

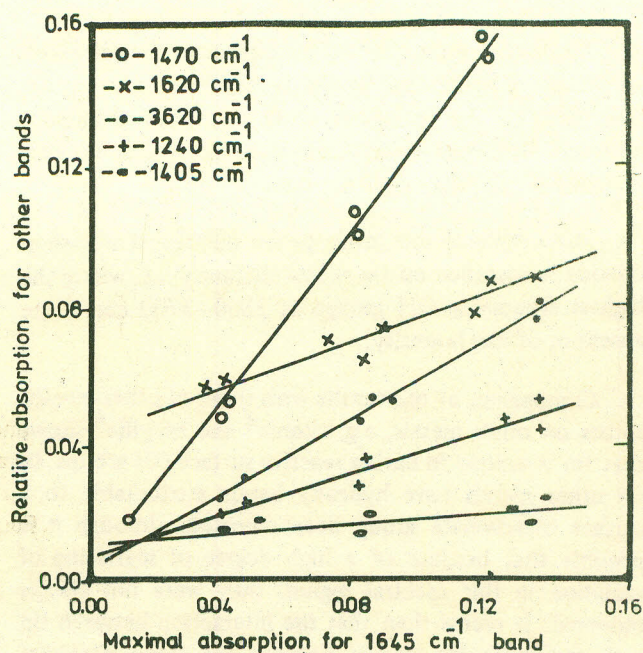


Fig. 5. Peak intensities of absorption bands of moist carbon dioxide-tin relative to the 1645 cm^{-1} band.

N.B. Since this figure depends (i.e. derived from fig. 4), it follows that this results from adsorption of moist carbon dioxide on tin after heating for three hours.

bands ($3620, 1645, 1470, 1240\text{ cm}^{-1}$) coupled with the fact that the lines of the 1620 and 1405 cm^{-1} do not pass through the origin would tend to rule out any appreciable contribution of the bicarbonate ion to the intensity of 1620 and 1405 cm^{-1} bands. This also support the assignment of these bands ($1620, 1405\text{ cm}^{-1}$) as the asymmetric and symmetric stretching frequencies of the adsorbed carboxylate groups.

Mechanism of Adsorption of Carbon Dioxide on Tin.

Different species resulting from the adsorption of carbon dioxide on addition of carbon dioxide gas to tin have been identified (Figs. 1–3). The bicarbonate groups are believed to be formed through an intermediate species, which absorbs at 1815 cm^{-1} , since its disappearance is accompanied by the simultaneous appearance of absorption bands at $3620, 1645, 1470, 1240\text{ cm}^{-1}$. This suggests the mechanism of formation of the bicarbonate as shown in the reaction Scheme No. 2. Consequently, the reactive OH groups are likely to be adjacent to the sites where carbon dioxide is initially adsorbed forming the carboxylate (structure VII a, Fig. 3) which absorbs at 1815 cm^{-1} . As these sites would seem to be vacant cationic sites, it would give more weight to Dunker and Fink's hypothesis that these represent hydroxy groups surrounded by four tin (Sn^{2+}) ions rather than to Peri's hypothesis³⁷ that they are surrounded by four oxide (O^{2-}) ions.

Although the surface bicarbonate group is shown in the reaction scheme 2 with a covalent bond between the

tin and oxygen atoms, infrared frequencies do not enable us to say whether the group is covalent or ionic, i.e. $-\text{Sn}^+\text{HCO}_3^-$. The spread of C—O absorption frequency amongst analogous compounds is so great that no firm conclusion can be drawn from them.

The results of this investigation indicate that carbon dioxide is adsorbed on tin at low alkalinity, i.e. where the highest frequency OH groups at $3800\text{--}3700\text{ cm}^{-1}$ are absent or of low intensity.

Comparison of our results with those of other investigators on other metals, e.g. titania⁴ and beryllia⁶ shows that tin is unique in having reactive surface OH groups. In no other metals have hydroxy bands attributable to a surface bicarbonate group been reported, although it is possible that because of a high degree of scattering of radiation in this spectral region, they were not always observed. It seems then that the interaction between tin and carbon dioxide occurs because tin alone possesses reactive OH groups immediately surrounding active initial adsorption sites. It is likely that these adsorption sites are of the Lewis base type (electron donors) (Fig. 3 structure VII a).

The infrared spectrum of tin sample heated in carbon dioxide at 150° for 3 hr is shown in Fig. 4. It is to be noted the appearance of absorption bands in the 1800 cm^{-1} region, namely at 1810 cm^{-1} in addition to the absorption bands at 1195 cm^{-1} . These values fall just outside those for the asymmetric C—O stretching frequency ($1620 \pm 20\text{ cm}^{-1}$) and symmetrical stretching frequency ($1275 \pm 25\text{ cm}^{-1}$) for the bidentate carbonate group^{32,33}. However, better agreement is obtained with the corresponding frequencies of organic carbonate: $1870\text{--}1750$ and $1280\text{--}1150\text{ cm}^{-1}$. Accordingly, the 1810 and 1195 cm^{-1} bands have been assigned to the asymmetric and symmetric stretching vibrations of the bridged structure shown in the reaction scheme 1, rather than to the bidentate structure. The possibility of contribution of a carboxylate species to the intensity of the band 1810 cm^{-1} is ruled out by the co-existence of the band at 1195 cm^{-1} which is the symmetrical stretching vibration of the bridged carbonate.^{32,33} Furthermore, the assignment of bands to surface carboxylate or to carbonate species can be, somewhat, safely based by studying the spectral region $1800\text{--}1200\text{ cm}^{-1}$. Carbonate absorbs in this region, where carboxylate does not. Consequently the existence of an absorption band at 785 cm^{-1} (Fig. 4) indicates a carbonate ligand since this band is usually assigned to the out of plane bending vibration of the bridged carbonate group⁴². It can be accounted for most of the reactions which occur when carbon dioxide is added to tin by the reaction Scheme No. 2.

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