

1037. *Addition Complexes between Stannic Chloride and Carboxylic Anhydrides.*

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Addition complexes between stannic chloride and acetic, propionic, and benzoic anhydrides have been prepared and characterised. They are high-melting solids with a 1 : 1 stoichiometry, and infrared measurements show that they probably have *cis*-chelated structures (I) and no acylium ion character. The characteristic carbonyl absorption frequencies of the anhydrides surprisingly undergo almost insignificant shifts on complex formation. In the aliphatic series increasing chain length leads to decreasing complex stability. The aliphatic complexes also undergo further decomposition reactions. The complex with benzoic anhydride is remarkably stable.

FEW studies exist of the interactions of metal halides with carboxylic anhydrides.¹ In view of the relevance to Friedel-Crafts acylation by anhydrides this is surprising. Two sorts of behaviour are known. In the first, typified by aluminium chloride-acetic anhydride, halogen replacement occurs (1) followed by other reactions. What little evidence is available suggests that this behaviour is common for the more reactive Lewis acids.¹ The second type of interaction involves adduct formation and no decomposition of the metal

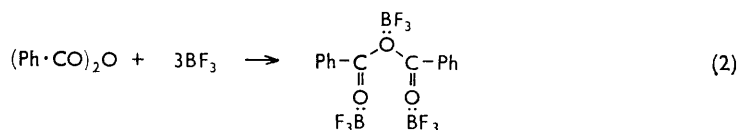


halide. There are perhaps only two clear-cut examples known,² both involving boron fluoride; one concerns benzoic and the other succinic anhydride. For the former the stoichiometry is $3\text{BF}_3:\text{1Bz}_2\text{O}$ and for the latter it is 1 : 1. In the few other relevant

¹ Olah, "Friedel-Crafts and Related Reactions," Interscience, 1963, Vol. I. See also Musso and Figge, *Annalen*, 1963, **668**, 1.

² Cook, *Canad. J. Chem.*, 1962, **40**, 445; Meerwein and Maier-Huser, *J. prakt. Chem.*, 1932, **134**, 51.

systems studied the evidence is conflicting, and the type of complex not yet unambiguously defined. In particular three different views of the nature of the acetic anhydride-boron fluoride reaction are available.¹



Infrared studies² lead to the conclusion that the benzoic anhydride complex contains no benzoyl cations, and may, perhaps, be represented as in scheme (2), though the spectrum is difficult to interpret.

In this Paper we describe complexes between tin chloride and anhydrides and discuss their structure in the light of infrared measurements.

EXPERIMENTAL

Materials.—All reagents were carefully purified and dried. Acetic and propionic anhydrides, distilled from magnesium when necessary, contained <1% of free carboxylic acid. They had b. p. 139 and 167°, respectively. Hexanoic anhydride, distilled from sodium, had b. p. 141°/14 mm. Benzoic anhydride, m. p. 42°, was dried *in vacuo*. Cyclohexane was dried by distillation from calcium hydride; Nujol by standing over sodium. Stannic chloride was redistilled under reduced pressure.

Preparation of Complexes.—Preparation and manipulation of the complexes were done in a dry box.

(i) *Complexes with acetic and propionic anhydride.* These were made by the slow addition of a calculated quantity of anhydride to the cooled (−15°) tin chloride. A white crystalline solid was formed in both cases. This solid eventually both liquefies and discolours, becoming dark brown. At room temperature this process takes over 24 hr. and below 0° is much slower. Discolouring is more rapid in the presence of excess of anhydride, or of any solvent in which the complex is appreciably soluble. Excess of anhydride is therefore to be avoided in the preparation, whenever possible. However, no matter what the proportions in which the reagents are mixed, any solid formed always has the same composition. This composition indicates a 1 : 1 stoichiometry. In practice the precipitated complex was freed from excess of stannic chloride (or anhydride) by repeated washing with cold cyclohexane (in which it is insoluble). Washing was followed by removal of any remaining volatile components *in vacuo*. The propionic complex appeared definitely less stable than that of acetic anhydride. It tended to liquefy under mechanical pressure, and to dissociate into the original reagents under reduced pressure. This lower complexing tendency for propionic, with respect to acetic, is in keeping with the fact that it was not found possible to prepare a solid complex from hexanoic anhydride.

The m. p.s of the acetic and propionic complexes (sealed tubes) were 215 and 145° (with decomposition) respectively.

(ii) *Complex with benzoic anhydride.* This was prepared by mixing solutions of the reagents in cyclohexane. The complex is a white powder, m. p. 81°, which is stable, even in moist air over long periods. The stoichiometry is 1 : 1 (see below).

Analysis of Complexes.—Weighed amounts were hydrolysed in dilute aqueous nitric acid and the resulting chloride titrated potentiometrically. Duplicate analyses were reproducible to within ±0.05% for the *benzoic anhydride complex*, which had a 1 : 1.00 mole ratio, within experimental error (Found: Cl, 29.09. Bz₂O, SnCl₄ requires Cl, 29.14%). The *acetic and propionic complexes* gave mole ratios of 1 : 0.95 and 1 : 0.97, respectively (Found: Cl, 37.18. Ac₂O, SnCl₄ requires Cl, 39.10%) (Found: Cl, 35.15. Pr₂O, SnCl₄ requires Cl, 36.29%). The slightly low chloride analyses are probably due to the decomposition noted above, which could lead to some non-hydrolysable chlorine.

Infrared Measurements.—These covered both the near and the far infrared regions. The former was studied with a Grubb-Parsons double-beam spectrometer with rock salt optics, and the latter with a Perkin-Elmer 221 spectrometer with caesium bromide optics. The spectra were taken (at *ca.* 25° and with cells which excluded moisture) either using liquid films, or mulls

in Nujol or cyclohexane, or a dilute solution in benzene. The aliphatic complexes tend to decompose in nujol and benzene. Details of the spectra are in the Tables. Observed frequencies were calibrated by comparison with a polystyrene spectrum.

RESULTS AND DISCUSSION

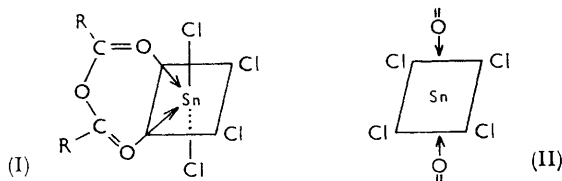
Stoichiometry.—This is 1 : 1 for all three complexes. The possibility that the observed 1 : 1 ratio really reflects an $x : x$ stoichiometry can, we feel, be rejected in view of the arguments which follow.

Far Infrared Spectra.—For stannic chloride and its derivatives, absorption in the 400 to 280 cm^{-1} region reflects the tin-chlorine motions. (Metal-ligand vibrations, even for the strongest donors, appear to lie beyond 280 cm^{-1} .) It seems possible in favourable cases to distinguish between 4-, 5-, and 6-co-ordinated structures.³ It is also possible to distinguish between *cis*- and *trans*-stannic chloride-two-ligand structures.³ For solution or liquid state spectra the observed absorptions will be reasonably diagnostic, but crystal-field effects in particular may sometimes lead to ambiguities for solid-state spectra. Our spectra were mostly taken for mulls of the solid complexes, but when possible solution spectra were also recorded. The solution and solid state spectra proved very similar. The observed absorptions (Table 1) suggest ³ *cis*-6-co-ordinated structures for we find two bands between 280 and 400 cm^{-1} (one intense and broad at 350—360 cm^{-1} and the other somewhat less intense at 300—310 cm^{-1}) and no significant absorption in the 400 cm^{-1} region for either the acetic or the benzoic anhydride complex.

The absence of absorption around 400 cm^{-1} appears to eliminate significant amounts of 4- and 5-co-ordinated tin,³ and the only remaining possibilities are thus *cis*- or *trans*-6-co-ordination. Of these the former (I), for good 1 : 1 stoichiometry, is the more sensible on general chemical grounds. The *trans*-structure (II) would imply a polymeric solid and different preparations might then be expected to lead to different analyses and melting points. This was not observed. The fact that the spectra are more like those expected for a *cis* structure than for a *trans* (which should have only one band between 280 and 400 cm^{-1}) is thus satisfactory. The data in Table 1 are, in fact, very similar in detail to those found for (supposedly) *cis chelated* nitrogen adducts of tin chloride.³

Acylium ion structures like $\text{RCO}^+[\text{SnCl}_4, \text{O} \cdot \text{COR}]^-$ seem unlikely on the basis of the far infrared spectra. As shown below the near infrared spectra rule them out.

The propionic complex is less stable (in particular as regards mulling) than those of the other anhydrides. In fact our spectra for this complex, while generally similar to those for the others, usually showed significant absorption at 400 cm^{-1} , thus revealing the probable presence of some free stannic chloride.



Near Infrared Spectra.—Expectations. (a) It has generally been concluded that complexes of anhydrides^{1,2} and (particularly) of esters⁴ with Lewis acids, involve co-ordination *via* the carbonyl group (rather than *via* the ethereal oxygen atoms). This conclusion seems reasonably established and, if *cis chelated* 1 : 1 structures are accepted for the present systems, carbonyl interaction is the only possibility.

Previous work^{1,4,5} on co-ordinated carbonyl groups shows the normal stretching

³ Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514; Beattie and Rule, *J.*, 1964, 3267. Zeil and Dietrich, *Z. phys. Chem.*, 1963, **38**, 36.

⁴ *E.g.*, Lappert, *J.*, 1961, 817; 1962, 542; Zackrisson and Lindquist, *J. Inorg. Nuclear Chem.*, 1961, **17**, 69.

⁵ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, 1960.

frequency to be reduced by 65—150 cm^{-1} on co-ordination to tin chloride. Carboxylic anhydrides have a pair of carbonyl absorptions.⁵ Our expectations were therefore that these would both be shifted. Cook reports as much for the $\text{Bz}_2\text{O}\cdot 3\text{BF}_3$ complex.²

TABLE 1.
Far infra-red absorptions ($400\text{--}280\text{ cm}^{-1}$).

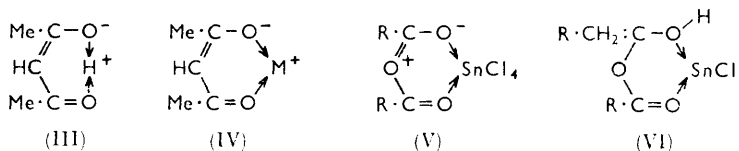
Complex	Frequencies (cm^{-1})
$\text{Bz}_2\text{O}\cdot\text{SnCl}_4$	{ 347vs, br; 294s (mull)
$\text{Ac}_2\text{O}\cdot\text{SnCl}_4$	{ 353vs, br; 304s (solution) *
$\text{Pr}_2\text{O}\cdot\text{SnCl}_4$	361vs, br; 310s
	357vs, br; 307s; (400) †

(vs = very strong, s = strong, m = moderate, w = weak, sh = shoulder, and br = broad in all Tables.)

* In benzene the complex dissociates somewhat, but its spectrum can be unambiguously determined in the presence of an excess of stannic chloride. † Corresponds to free SnCl_4 (see text).

The free anhydrides do not absorb in this region at the film thicknesses used. The benzoic complex was mull in Nujol, the others in cyclohexane.

(b) Acetylacetone (because of its cyclic hydrogen-bonded structure) and metal acetylacetonate complexes exhibits unusually intense absorption (*ca.* 100 times that usual for normal carbonyl bands) at $1640\text{--}1540\text{ cm}^{-1}$. Another band appears between 1520 and 1320 cm^{-1} . The first band has been attributed to the reduction of the carbonyl stretching frequency implicit in (III) and (IV); a formal single C—O bond appears in each.



The β -diketo unit of acetylacetonate (which leads so readily to complexes based on a 6-membered ring) is, of course, also present in anhydrides, and this is a further strong reason for accepting their *cis* chelation to stannic chloride. To what extent we were to expect structure (I) to provide phenomena similar to those noted for (III) and (IV) was not clear. Contributions from forms like (V) might, however, sensibly be expected to provide similar effects. Any enolisation of the α -hydrogen atoms in the aliphatic anhydrides could also lead to somewhat analogous structures (VI). These enolised forms should also provide O—H absorption.

Findings.—These are in Tables 2, 3, and 4. We deal with those for the benzoic anhydride complex first. The main effects are: (1) The carbonyl bands of the anhydride are very slightly shifted in the complex. Their relative intensities are somewhat altered, but their general intensity is very similar to that in the free anhydride. (Our mulls were

TABLE 2.
Near infrared absorptions for the benzoic anhydride system (cm^{-1}).

Bz_2O	$\text{Bz}_2\text{O}\cdot\text{SnCl}_4$	Comments	Bz_2O	$\text{Bz}_2\text{O}\cdot\text{SnCl}_4$	Comments
1767s	1776m	C=O stretch $\Delta\nu = +9\text{ cm}^{-1}$	1033vs	1048 vs	$\Delta\nu = +15\text{ cm}^{-1}$
1704m	1689s	C=O stretch $\Delta\nu = -15\text{ cm}^{-1}$	1010vs	1018vs	
—	1621s	(VI) ?	992s	995s	
1592m	1600s		934w	943vw	
—	1574s	(VI) ?	873vw	873vw	
1311w	1317vw		775m	787m	$\Delta\nu = +12\text{ cm}^{-1}$
1279w	1284vw		704vs	711vs	
1208vs	1211vs		685m	683w	
1168s	1171s		—	673w	(I) or (V)
1099vw	1103vw		—	664w	(I) or (V)
1068w	1072m				

Spectra taken as mulls in Nujol. Nujol bands omitted. Frequencies reproducible to $\pm 5\text{ cm}^{-1}$ in Tables 2, 3, and 4.

TABLE 3.

Near infrared absorptions for the acetic anhydride system (cm^{-1}).

Ac_2O	$\text{Ac}_2\text{O}, \text{SnCl}_4$	Comments	$\text{Ac}_2\text{O}, \text{SnCl}_4$ (decomp.)	Ac_2O	$\text{Ac}_2\text{O}, \text{SnCl}_4$	Comments	$\text{Ac}_2\text{O}, \text{SnCl}_4$ (decomp.)
—	3106m	O—H stretch?	3077s, br	1222m	1263m	$\Delta\nu = +41 \text{ cm}^{-1}$	1250s, br
1812vs	1815vs	C=O stretch	1802vw	1122vs	1125vs		1130w
1788s, sh	1746s, sh	C=O stretch	—	1042w	1044w		1042m
1748s	1748m	C=O stretch	—	994s	998s		1014m
—	1634vs, br	(VI)?	1626vs, br	—	951w	(I) or (V)	—
—	1504vs	(VI)?	—	895s	904m		904m, br
—	1475vs	(VI)?	1466s	780w	785w		—
1420m	1401m, sh	$\Delta\nu = -19 \text{ cm}^{-1}$	1395s, br	—	725s	(I) or (VI)	721s
1366s	1362s	—	—	—	688m	(I) or (VI)	—

Ac_2O as liquid film; complexes as mulls in cyclohexane. Cyclohexane bands omitted. Similar remarks apply for Table 4.

TABLE 4.

Near infrared absorptions of the propionic anhydride system (cm^{-1}).

Pr_2O	$\text{Pr}_2\text{O}, \text{SnCl}_4$	Comments	Pr_2O	$\text{Pr}_2\text{O}, \text{SnCl}_4$	Comments
—	3165m	O—H stretch?	1263w	—	
2941m	2941m?	{ obscured by cyclohexane,	—	1224m	(I) or (VI)
2875m	2875m?		1131m, sh	1103s	$\Delta\nu = -28 \text{ cm}^{-1}$
1802vs	1799s	C=O stretch	1091s, br	1075vs, br	$\Delta\nu = -16 \text{ cm}^{-1}$
1739s	1742s	C=O stretch	1038vs, br	1041vs, br	
1631vw	1634vs, br	(VI)?	1005m, sh	1005m, sh	
—	1481vs	(VI)?	—	924m	(I) or (VI)
1453m	1458s		—	912m, br	(I) or (VI)
1410m	1401s	$\Delta\nu = -9 \text{ cm}^{-1}$	853vw, br	851w, br	
1377w	1376m		803,w br	809s	
1342m	1342w		—	707m, br	(I) or (VI)
—	1295s	(I) or (VI)	—	692m, br	(I) or (VI)

not quantitative and these judgements are based on comparisons with other regions of the spectra.) (2) The spectrum of the complex also contains the majority of the other bands characteristic of the free anhydride. They are all very little shifted. (3) Certain new bands appear for the complex. Notably those at 1621, 1574, 673, and 664 cm^{-1} . (4) There are no bands in the 2200 cm^{-1} region.

The benzoic complex is remarkably stable and, in view of the data for the far infrared region, certainly does not contain significant free tin chloride. It cannot therefore contain much free benzoic anhydride. Because of this fact, and of result (1) above, we conclude that this example of carbonyl co-ordination involves an unusually small shift of the carbonyl absorption frequency. That carbonyl interaction is indeed involved is indicated by the change in the relative intensities of the twin bands on going from the free anhydride to the complex.

Of the new bands those at 1621 and 1574 cm^{-1} are the most interesting. These are not due to free, or complexed, benzoic acid (from some hydrolysis) for there is no evidence of O—H absorption. Nor can they be accounted for by free, or complexed benzoyl chloride.⁶ These bands might represent the shifted carbonyl absorptions but the situation cannot be so simple because of the strength of the absorptions in the 1700 cm^{-1} region. We tentatively attribute these new bands to contributions from a small amount of a strongly absorbing structure like (V). Yet since the carbonyl stretching absorptions of the complex have already been accounted for, we must assign the absorptions at 1621 and 1574 cm^{-1} to some other motions of the 6-membered cyclic structures resembling (IV). This conclusion seems relevant to the interpretation of the spectra of acetylacetone complexes themselves.⁵

There seem at least two possible reasons for the absence of the expected frequency shifts. (a) The interaction is, in this case, much weaker than that in the tin chloride

⁶ Hunt and Satchell, unpublished observations.

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complexes with ketones and esters previously studied. This appears rather unlikely. (b) The change in carbonyl frequency on co-ordination is thought to be compounded of two opposing effects. The concomitant bond weakening leads to a decreased frequency,^{4,5} but a mechanical effect⁷ leads to a shift in the opposite direction. In previous work on co-ordination at oxygen, the latter effect has usually appeared the smaller of the two.¹ Perhaps, however, with *cis* chelated anhydrides the two opposing effects are nicely balanced. Perhaps also other factors contribute, and that such a simple model is inadequate.⁸

A final point concerns result (4). This rules out significant contributions from acylium ion structures.^{1,9} A similar result and conclusion also applies for the complexes of acetic and propionic anhydride, to which we now turn. The other main features here are: (1) Strong, essentially unshifted carbonyl bands remain in both complexes. (2) In the acetic complex the majority of the other bands typical of the anhydride also remain rather a little affected, either in intensity or in position, save for that at 1222 cm.⁻¹, which shifts to 1263 cm.⁻¹. For the propionic complex most of the bands are again retained, though here more than one of them is detectably shifted. The perturbations are small. (3) For both complexes certain new bands appear. As the Tables show, the new long-wavelength bands appear as double absorptions for propionic anhydride. They are perhaps therefore associated with C-C motions in the complex. The absorptions around 3100 cm.⁻¹ and at 1634 and 1500–1475 cm.⁻¹ are the most interesting of the new bands. The moderate absorptions around 3100 cm.⁻¹ probably signify some O-H content for the specimens. (These bands do not appear to be obvious overtones.) The absorptions at 1634 and 1500 cm.⁻¹ are very intense. They are reminiscent of the bands found for acetyl-acetone complexes. Yet our carbonyl frequencies are already accounted for. Recalling our discussion of the benzoic complex, we tentatively postulate that the complexes are predominantly (I) but contain a small amount (some few percent.) of structure (VI). Some contribution from structures like (V) may also be involved.

The new bands could perhaps be due to very strongly adsorbing decomposition products. For various reasons (concerning their intensities, their exact positions, and the absence of certain other frequencies) the new bands cannot be attributed to free, or complexed, carboxylic acid or acid chloride.⁶ They could,⁵ however, be due to condensation products, such as CH₃·COCH₂·CO·O·COCH₃. No doubt these, and other more elaborate derivatives, are eventually formed. (The complexes eventually darken and liquefy.) However, since the various condensation products very probably arise *via* structures like (VI), we feel that the assumption that the solid complexes contain small amounts of species like (VI) is justified, even if aged samples contain other β-diketo species also.

The possibility of structures like (VI) for the aliphatic anhydrides and their impossibility for aromatic anhydrides, provides a reasonable explanation of the differences in ageing effects for the two classes. Keto-complexes with available α-hydrogen atoms often appear to react further.¹

Therefore both the near and the far infrared spectra are compatible with the presence of a chelated unit. These particular anhydride complexes are, of course, the first studied to involve a Lewis acid capable of this type of co-ordination.

The marked tendency of the aliphatic complexes to decompose further, especially when in contact with a solvent, has obvious serious implications for preparative scale acylation in systems of this type.

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⁷ Overend and Scherer, *J. Chem. Phys.*, 1960, **32**, 1296.

⁸ Beattie and Gilson, *J.*, 1964, 2292.

⁹ Susz and Wuhmann, *Helv. Chim. Acta*, 1957, **40**, 722, 971.