

CATALYTIC SYSTEMS LEWIS ACID-BRÖNSTED ACID: INFRARED AND PMR SPECTROSCOPIC STUDY

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Interactions in catalytic systems Lewis acid (TiCl_4 , SnCl_4) and carboxylic acid (CF_3COOH , CCl_3COOH , CF_2HCOOH , CCl_2HCOOH , CH_3COOH , $\text{CH}_3\text{CH}_2\text{COOH}$, $(\text{CH}_3)_3\text{CCOOH}$) in benzene, 1,2-dichlorobenzene, and n-heptane were investigated by means of infrared and PMR spectroscopy. In studying reactions of TiCl_4 with carboxylic acids it was found that both the complex $\text{TiCl}_4 \cdot \text{RCOOH}$ and the carboxylate RCOOTiCl_3 (and HCl) were formed. With the decreasing strength of the acid the fraction of the complex increases; with the increasing strength of the acid the fraction of the carboxylate increases, but the fraction of the acid entering into the reaction with TiCl_4 decreases. SnCl_4 does not observably interact with either tri- or dihalogenated acids, while with non-halogenated acids it forms complexes $\text{SnCl}_4 \cdot 2 \text{RCOOH}$. For these complexes equilibrium constants of their formation in benzene and 1,2-dichlorobenzene were determined.

Lewis acids react with carboxylic acids to form complex compounds¹ of higher acidity than the original acids. For this reason, the systems Lewis acid-carboxylic acid were often used as catalysts of cationic oligomerizations and polymerizations of olefins^{2,3}. These catalysts contained most often TiCl_4 or SnCl_4 as the Lewis acids and halogenated aliphatic acids^{4,5}. Methods of physical chemistry were used to investigate the interactions of components in systems containing stannic chloride. Thus, the formation of complexes of SnCl_4 with non-halogenated aliphatic acids and a rather weak interaction with monohalogenated acids was proved by measuring changes in electrical conductivity, density, and viscosity during mixing of the components^{6,7}. Studies of infrared spectra have shown that the formation of these complexes is due to the electron-donor bond of the oxygen of the carboxylic C=O bond to the Lewis acid⁸. The donation of an electron leads to a lowering of the wavenumber of the $\nu(\text{C}=\text{O})$ vibration usually accompanied by an increase of the wavenumber of the $\nu(\text{C}-\text{O})$ vibration⁹. Satchell and Wardell¹⁰ observed that SnCl_4 formed complexes $\text{SnCl}_4 \cdot 2 \text{RCOOH}$ with non-halogenated acids, and determined their equilibrium constants of formation in 1,2-dichlorobenzene. Little is known about the interaction of TiCl_4 with carboxylic acids except that carboxylates are formed by warming TiCl_4 with non-halogenated carboxylic acids¹¹ and that $(\text{CF}_3\text{COO})_2\text{TiO}$ is formed by boiling TiCl_4 with CF_3COOH for hundreds of hours¹².

Titanium tetrachloride in combination with carboxylic acids often differs considerably in its properties and in its catalytic activity from the catalysts containing stannic chloride. Therefore, we have investigated in this study interactions in both systems using both halogenated and non-halogenated aliphatic carboxylic acids with the help of infrared and PMR spectroscopy. The aim of this work was to find out,

if possible in a quantitative way, the products of interaction of the components of the particular systems and thus to provide a basis for the interpretation of their catalytic activity. Besides that, the knowledge of interaction mechanisms of the catalytic components is important in formulating the over-all kinetic pattern of oligomerization or polymerization.

EXPERIMENTAL

Chemicals. TiCl_4 and SnCl_4 (Fluka) were distilled *in vacuo*. CF_3COOH and CCl_2HCOOH (Koch-Light), CCl_3COOH , and CF_2HCOOH (Fluka) were distilled under nitrogen and only the middle fractions were used. Acetic and propionic acid were boiled with small amount of their anhydrides and only the middle fraction was collected during distillation. The portion of pivalic acid which crystallized at the room temperature was used. All substances were kept in ampules under nitrogen. From weighed amount of acids concentrated solutions in benzene, n-heptane, 1,2-dichlorobenzene, and *p*-xylene were prepared immediately before being used. Benzene, n-heptane, and *p*-xylene were dried by refluxing for eight hours with LiAlH_4 (1,2-dichlorobenzene with CaH_2) and distilled.

Preparation of catalytic systems. Concentrated solutions of the acid, the solvent, and the Lewis acid were mixed under nitrogen by means of syringes. In preparation of the systems with titanium tetrachloride, hydrogen chloride was evolved and the sample-tubes were therefore firmly closed only after the evolution was over. The following systems were prepared for the infrared measurements: TiCl_4 with CF_3COOH , CF_2HCOOH , CCl_3COOH , CCl_2HCOOH , CH_3COOH , $\text{CH}_3\text{CH}_2\text{COOH}$; SnCl_4 with CF_3COOH , CCl_3COOH , CH_3COOH , $\text{CH}_3\text{CH}_2\text{COOH}$, $(\text{CH}_3)_3\text{C}\cdot\text{COOH}$. In heptane only TiCl_4 with CF_3COOH and CCl_3COOH were prepared, as heterogeneous systems were formed with the other acids. In benzene and 1,2-dichlorobenzene precipitation of products occurred in the systems TiCl_4 -non-halogenated acids, at the ratio TiCl_4 : $\text{RCOOH} < 1$; therefore, these systems were studied only for the component ratios TiCl_4 : $\text{RCOOH} \geq 1$. Complexes of SnCl_4 and non-halogenated acids in heptane separated out as a heavier liquid phase; in benzene and 1,2-dichlorobenzene they were soluble.

Infrared spectra were measured using a Zeiss (Jena) UR-10 spectrometer in the range 400 to 3800 cm^{-1} . Potassium bromide cells (0.06–0.1 mm) were filled up in nitrogen atmosphere with the help of syringes. The concentration of acids in the measured systems was kept about 0.3M (m.w. of the monomer acid). The ratio of TiCl_4 or SnCl_4 to the acid was changed between 0.5 and 5. Absorption of the solvent was compensated by means of a variable thickness cell. Free acid in the catalytic system measured immediately after the calibration was determined from the calibration curve of the pure carboxylic acid. PMR spectra were measured of the systems TiCl_4 with CF_3COOH , CCl_3COOH , CH_3COOH ; and SnCl_4 with CF_3COOH , CH_3COOH , $(\text{CH}_3)_3\text{C}\cdot\text{COOH}$, and the particular acids in benzene. Initial concentrations of the acids were 4.5M, the molar ratio Lewis acid-carboxylic acid varied between 0 and 2. The system TiCl_4 with CH_3COOH was studied at the ratio TiCl_4 : $\text{CH}_3\text{COOH} \geq 0.9$. Solutions of the carboxylic acids in benzene were measured in the concentration range 0.5–5M. Preparation procedure of the samples for the PMR spectra measurements was the same as for the infrared spectra. The PMR spectra were measured at 80 MHz using a Tesla BS 487 spectrometer with the proton stabilization at 25°C and with tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

INFRARED SPECTRA

In the systems TiCl_4 or SnCl_4 with carboxylic acids the concentration decrease of the carboxylic acid was followed quantitatively by infrared spectroscopy. With all acids and in all solvents, with the exception of CF_3COOH and CCl_3COOH in benzene, the absorption band $\nu(\text{C}=\text{O})$ of the acid dimer was employed for this purpose. The dissociation dimer–monomer increases with the increasing strength of the acid, with the increasing basicity of the solvent, and with the decreasing concentration of the acid. Therefore, the calibration curves of the dimer bands used are not linear, especially in the region of low acid concentrations. In the cases of CF_3COOH and CCl_3COOH in benzene the average value of the intensity of the dimer and monomer $\nu(\text{C}=\text{O})$ absorption band was used to determine the acid concentrations. The wavenumbers of the $\nu(\text{C}=\text{O})$ vibrations of both monomers and dimers of all the acids are shown in Table I. When comparing the intensity ratios of the dimer and monomer bands in the calibration measurements with those of the catalytic systems, it was found that the dimer–monomer equilibrium was determined by the concentration of the free acid in the solvent, and it was not influenced by the presence of either the unreacted Lewis acid or the interaction products at the given concentration conditions. In the case of the strong acids CF_3COOH and CCl_3COOH in the basic solvent (*e.g.*, in aromatics) and at higher concentrations of the Lewis acid one should take into consideration the dilution of the solvent by the Lewis acid and by products of

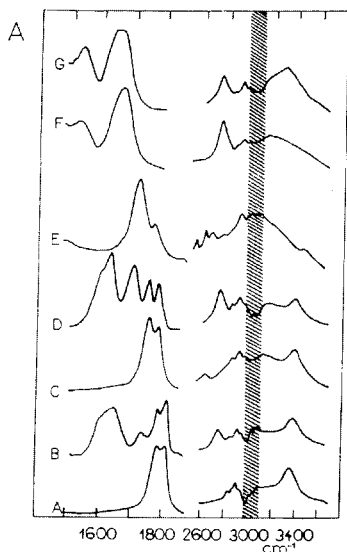


FIG. 1

Infrared Spectra of Catalytic Systems TiCl_4 - RCOOH in Benzene

A CF_3COOH (0.25M); B CF_3COOH : $\text{TiCl}_4 = 1 : 5$, initial concentration $[\text{CF}_3\text{COOH}]_0 = 0.25\text{M}$; C CCl_3COOH (0.4M); D $\text{CCl}_3\text{COOH} : \text{TiCl}_4 = 1 : 1$, $[\text{CCl}_3\text{COOH}]_0 = 0.4\text{M}$; E CH_3COOH (0.5M); F $\text{CH}_3\text{COOH} : \text{TiCl}_4 = 1 : 2$, $[\text{CH}_3\text{COOH}]_0 = 0.5\text{M}$; G $\text{CH}_3\text{COOH} : \text{TiCl}_4 = 1 : 5$, $[\text{CH}_3\text{COOH}]_0 = 0.5\text{M}$. Cell thickness 0.07 to 0.1 mm, absorption of benzene compensated.

its interaction; this leads to a decrease in the solvation action of the solvent which causes the dissociation of the dimer. The products of interaction of the Lewis acids with the protonic acids are in all cases characterized by a lower wavenumber of the $\nu(\text{C}=\text{O})$ vibration than the monomer or the dimer, and thus they do not interfere in the determination of the free acid.

Titanium tetrachloride-carboxylic acids. Results of the infrared spectroscopic investigation of the interaction TiCl_4 with the carboxylic acids are summarized in Table I. The data on the amount of the reacted acid at selected ratios $\text{RCOOH}/\text{TiCl}_4$ show that weak non-halogenated acids reacted practically quantitatively even at the component ratio 1 : 1, while in the systems containing strong halogenated acids both non-reacted acids and TiCl_4 remained in the solution (Fig. 1). In the systems with weak acids the reaction — accompanied by hydrogen chloride evolution — was over in a few minutes. In the systems with strong acids a rapid evolution of hydrogen chloride occurred during the first several minutes, but a slower evolution continued then for a long time. Therefore, the infrared spectra of samples of the catalytic systems were measured usually after 30–50 minutes after the mixing. A comparison with the conversion of the acid after 20 hours for the systems in 1,2-dichlorobenzene is shown in Table I. Also, it can be seen from the data in this table, how the nature of the solvent influenced the interaction of the components. In heptane in the systems with weaker acids precipitation of the products occurred, in the systems with strong acids a substantially larger amount of the acid reacted than in the more polar 1,2-dichlorobenzene or in the more basic benzene. The differences in the reacted amount of acids in 1,2-dichlorobenzene and benzene are not large, though both solvents influence the reacting components in a different way.

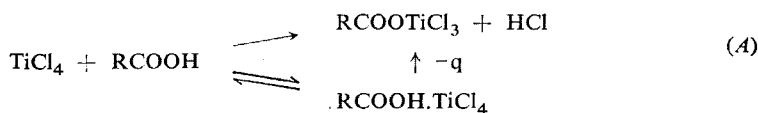
The decrease of the intensity of $\nu(\text{C}=\text{O})$ acid bands in the systems containing TiCl_4 and RCOOH : $\text{TiCl}_4 = 1$ was accompanied by the increase of the intensity of two new bands with the wavenumbers by 150 cm^{-1} and 50 cm^{-1} , respectively, lower than the band of the same vibration of the acid dimer. The bands shifted by 150 cm^{-1} were assigned to the $\nu(\text{C}=\text{O})$ vibration of carboxylates RCOOTiCl_3 whose formation is bound to the evolution of hydrogen chloride. The evolving gas was identified as HCl by the precipitation of AgCl from the aqueous solution of AgNO_3 . Also, hydrogen chloride dissolved in the reaction mixture showed a characteristic absorption at 2750 cm^{-1} . The presence of carbon dioxide in the evolved gas was not proved, neither chemically ($\text{Ba}(\text{OH})_2$) nor in the infrared spectra of either the liquid or the gas. The correct interpretation of the shifted $\nu(\text{C}=\text{O})$ band was confirmed in several instances by measuring carboxylates prepared in other ways. The carboxylates prepared by the reaction of RCOONa with an excess of TiCl_4 in benzene gave in their infrared spectra a strong absorption at the wavenumbers very close to the wavenumbers of the above mentioned band in the systems with the corresponding acids.

TABLE I
Results of Infrared Analysis of Catalytic Systems $\text{TiCl}_4\text{-RCOOH}$

R	$\nu(\text{C=O}), \text{cm}^{-1}$ (in benzene)			
	$(\text{RCOOH})_2$	RCOOH	$\text{TiCl}_4\cdot\text{RCOOH}$	RCOOTiCl_3
CF_3	1 784	1 810	1 730	1 615 ^f 1 640
CCl_3	1 755	1 784	1 705	1 610 ^f 1 630
CF_2H	1 765	1 790	1 712	1 625
CCl_2	1 745	1 780	1 695	1 590 ^f 1 615
CH_3	1 717	1 760	1 640 ^f 1 660	1 530
CH_3CH_2	1 715	1 755	1 620 ^f 1 650	1 530

^a Percent of amount of acid added to the system; ^b A(X), A(Y) areas of bands of $\nu(\text{C=O})$ vibrations of complex and carboxylate; ^c molar ratio $\text{RCOOH} : \text{TiCl}_4$; ^d values obtained after 20 hours of aging the catalyst at room temperature; ^e 1,2-dichlorobenzene; ^f absorption bands appearing at $\text{RCOOH}/\text{TiCl}_4 < 1$.

The $\nu(\text{C=O})$ bands shifted by 50 cm^{-1} were assigned to the complexes $\text{RCOOH}\cdot\text{TiCl}_4$, as during heating of the catalytic systems their intensity decreased while the intensity of the carboxylate bands increased with a simultaneous evolution of HCl . As a result of these observations the interaction of TiCl_4 with acids can be characterized by equation (A):



The stoichiometric composition of the complex and the salt was proved in the systems with non-halogenated acids. In the reaction of acetic acid and propionic acid with TiCl_4 (1 : 1) practically all free acid and all TiCl_4 was consumed. In an excess of the acid a precipitate of a mixture of the complex and the carboxylate was formed and the excess acid remained in the solution. The excess of TiCl_4 above the 1 : 1 ratio showed itself in the band of the free TiCl_4 at 490 cm^{-1} . Because TiCl_4 prefers¹³ the formation of complexes with the component ratio 1 : 1 with carboxylic and carbonyl compounds, and because the shift of the $\nu(\text{C=O})$ vibration of the complex is constant with respect to the position of the $\nu(\text{C=O})$ band of the free acid, it may be assumed that even stronger acids form complexes with TiCl_4 with the 1 : 1 component ratio.

TABLE I
(continued)

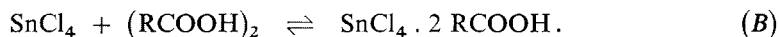
Reacted acid, % ^a								A(X) : A(Y) ^b			
heptane		benzene		DCB ^e				benzene		DCB ^e	
1 : 1 ^c	1 : 5 ^c	1 : 1 ^c	1 : 5 ^c	1 : 1 ^c	1 : 1 ^{cd}	1 : 5 ^c	1 : 5 ^{cd}	1 : 1 ^c	1 : 5 ^c	1 : 1 ^c	1 : 5 ^c
66	72	15	25	—	15	24	55	0.05	0.1	0.2	0.3
82	86	54	79	82	88	86	96	0.7	0.6	0.6	0.7
—	—	75	89	84	—	93	—	0.7	0.7	0.5	0.7
97	100	80	93	70	90	88	96	0.8	0.7	1.1	1.0
—	—	100	100	100	—	100	—	2.2	1.3	2.5	1.7
—	—	100	100	100	—	100	—	2.4	1.6	2.3	1.7

For the component ratios $\text{RCOOH} : \text{TiCl}_4 > 1$ further $\nu(\text{C}=\text{O})$ bands appear which are shifted by $20-30 \text{ cm}^{-1}$ towards lower wavenumbers in comparison with the bands found at the 1 : 1 component ratio for carboxylates of strong acids and complexes of weak acids (Table I). Both these effects can be explained by solvation by TiCl_4 of both the $\text{C}=\text{O}$ bonds in carboxylates and the $\text{C}-\text{O}$ bonds in complexes. These phenomena make it practically impossible to quantitatively evaluate the amount of the complexes and carboxylates formed, as the extinction coefficients of these bands are considerably dependent on the concentration of TiCl_4 and, moreover, pure complexes for calibration purposes were not prepared. However, because the contents of the complexes and the carboxylate should determine to some extent the catalytic activity of the particular systems, the areas of the peaks of the complex (A(X)) and the carboxylate (A(Y)) were evaluated. This procedure would be justified, if the extinction coefficients of the complex bands and the salt bands did not differ much from each other, if they changed in a similar way with the electronegativity of the acid alkyl, and if they were not influenced by the excess of TiCl_4 . As at least the last assumption is not satisfied, the data summarized in Table I can serve only as a rough estimation of the relative abundances of both products in the systems. However, it follows from them quite clearly that the tendency of acid to form complexes with TiCl_4 increases with the decreasing strength of the acid, and that strong acids react with TiCl_4 to form more carboxylate, while the complex is formed to a lesser extent only. The excess of TiCl_4 supports the formation of the carboxylate in the systems with weak acids, while in those systems with strong acids which contain also the free acid, the effect of the TiCl_4 excess on the abundance of both products is not obvious (Table I). Aging of the catalytic systems does not have a significant

effect on the ratio complex-carboxylate, even though the amount of the free acid in the systems with strong acids decreases in time. Also, the differences in the properties of benzene and 1,2-dichlorobenzene are not sufficient to influence unambiguously the distribution of the acid between the complex and the carboxylate. The only exception in this sense represents the system $\text{CF}_3\text{COOH-TiCl}_4$ (Table I).

The interpretation of further absorption bands in the spectra of the catalytic systems has not yet been possible, with the exception of the bands of the $\nu(\text{O-H})$ vibration in some systems. This was because always the spectra of the mixtures of complexes and carboxylates, or non-reacted acids in the dissociation equilibrium dimer-monomer were obtained. Moreover, the spectra of complexes and carboxylates were influenced in some cases by the excess of TiCl_4 . The interpretation of the molecular spectra of acids is complicated by coupling of some vibrations, and thus the calculation of normal vibrations and potential energy distributions made it possible to interpret completely only the molecular spectra of the acetic acid monomer and dimer¹⁴. If a complex is formed, all vibrations of the carboxylic group are changed as well as the vibrations of the alkyl groups coupled with them. The dominant change in the spectra of acids, when complexes and carboxylates are formed, is the shift of the strong band of the asymmetric stretching vibration C-C-O coupled with the bending vibration C-O-H (which lies in $(\text{CH}_3\text{COOH})_2$ at 1295 cm^{-1} , in CH_3COOH at 1190 cm^{-1} (ref.¹⁴), in $(\text{CCl}_3\text{COOH})_2$ at 1260 cm^{-1} , in CCl_3COOH at 1155 m^{-1} , in $(\text{CF}_3\text{COOH})_2$ at 1235 cm^{-1} , and in CF_3COOH at 1130 cm^{-1}) to the region 1400 cm^{-1} . In this region there lies also the asymmetric stretching vibration C-C-O of carboxylates and bands of the bending vibrations of the C-H bonds; this all made it impossible to identify the absorption band of the above mentioned vibration of complexes.

Stannic chloride-carboxylic acids. Stannic chloride did not show any interaction with halogenated acids. With weak acids, as, e.g., CH_3COOH , $\text{CH}_3\text{CH}_2\text{COOH}$ and $(\text{CH}_3)_3\text{CCOOH}$, it formed complexes 2 : 1 as observed earlier.¹⁰ These complexes can be prepared pure in heptane. The complexes separate out as a heavier liquid phase; in their infrared spectra no free acid was observed. If the complex prepared in this way was dissolved in benzene or 1,2-dichlorobenzene, a well-observable dissociation of the complex occurred. Also, if the components of the system were mixed together in benzene or 1,2-dichlorobenzene, the formation of the complex according to equation (B) occurred, up to the equilibrium



The complexes are characterized by a decrease of the wavenumber of the $\nu(\text{C=O})$ band roughly by 80 cm^{-1} in comparison with the dimer (Table II). These bands are not suitable for analytical purposes, because of their width and asymmetry.

In the interaction of the components no side reaction occurs (*e.g.*, hydrogen chloride release). Assuming the composition of the complex is independent of the initial ratio of the components, the equilibrium constant of equation (B) can be obtained. The calculation can be made, if the initial concentrations of the components and the equilibrium concentration of the acid (obtained in the infrared analysis) are known. The error in the calculation arising from neglecting the dimer-to-monomer dissociation is for aliphatic acids of the order of 10^{-3} (ref.¹⁰). The equilibrium constants summarized in Table II agree well with the values reported by Satchell and Wardell¹⁰ for 1,2-dichlorobenzene, even though our values were obtained at an order-of-magnitude higher concentrations. The values of the equilibrium constants increase with the decreasing strength of the acid in the case of both 1,2-dichlorobenzene and benzene, but they are consistently lower in the more basic benzene.

It is remarkable that increasing the ratio $\text{SnCl}_4 : \text{RCOOH}$ over 0.5 leads to a considerable change in the intensity of bands of the complex and an increase of the band shoulder of the $\nu(\text{C}=\text{O})$ vibration of the complex at about 20 cm^{-1} higher wavenumber. At the same time, a broad absorption band with a maximum at 3330 cm^{-1} increases which overlaps a broad absorption band of the $\nu(\text{O}-\text{H})$ vibration of the complex $\text{SnCl}_4 \cdot 2 \text{RCOOH}$ with a maximum at 3140 cm^{-1} . Interpretation of other absorption bands of the complex was not carried out for the same reasons as stated for the systems with TiCl_4 .

Vibration $\nu(\text{O}-\text{H})$ in acids and complexes. Dimers of all aliphatic acids both in the gaseous phase and in solvents exhibit a broad absorption with numerous maxima in the region $2500-3150 \text{ cm}^{-1}$ (ref.^{15,16}). The extreme width of the $\nu(\text{O}-\text{H})$ bands of the dimers was explained both by the Fermi resonance, and by the coupling of the high-frequency and low-frequency vibrations of the hydrogen bond¹⁷. In solutions

TABLE II
Characteristic Features of Complexes $\text{SnCl}_4 \cdot 2 \text{RCOOH}$

R	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$	Equilibrium constant of formation ^a	
		benzene	1,2-dichlorobenzene ^b
CH_3	1 640, 1 655 sh ^c	7.5	12 (20)
CH_3CH_2	1 630, 1 640 sh ^c	10	17 (43)
$(\text{CH}_3)_3\text{C}$	1 620, 1 640 sh ^c	56	130 (112)

^a Concentration of acids 0.166M (dimer), ratio $\text{SnCl}_4/\text{RCOOH}$ 0.5-5; ^b values in parentheses from ref.¹⁰; $[\text{RCOOH}] = 10^{-2}-10^{-1}\text{M}$, $[\text{SnCl}_4] = 10^{-3}-10^{-1}\text{M}$; ^c appears in an excess of SnCl_4 , sh shoulder.

a dissociation of the dimer to the monomer, and possibly even to linear oligomers occurs¹⁸. While isolated molecules of the monomer in the gaseous phase have practically the same wavenumber of the $\nu(\text{O—H})$ band in CF_3COOH (3587cm^{-1}) and CH_3COOH (3581cm^{-1}) (ref.¹⁵), with increasing basicity of the solvent the wavenumber of this band decreases in strong acids much more than in weak acids¹⁹. This is caused by a stronger solvation of the more acidic hydrogen of the monomer acid by basic (*e.g.*, aromatic) solvents. Table III shows the wavenumbers of the $\nu(\text{O—H})$ vibrations of acid monomers measured in the solvents whose basicity increases in the sequence 1,2-dichlorobenzene, benzene, *p*-xylene.

In the complexes of acids with Lewis acids the increase of the hydrogen acidity is assumed which results from the O—H bond polarization caused by the shift of the electron density from the carboxyl towards the electron-donor bond. The wavenumber of the $\nu(\text{O—H})$ vibration of these complex acids ought to be lower in comparison with the vibrations of the monomer acids in the aromatic solvents used by us, as a result of a higher acidity of the hydrogen.

In the systems of non-halogenated acids with TiCl_4 and SnCl_4 one or two broad absorption bands (Table III) appear in the region of the $\nu(\text{O—H})$ vibrations, depending on the ratio of the components. The first band with a maximum at about 3150cm^{-1} appears at the component ratio $\text{RCOOH} : \text{TiCl}_4 = 1$, and $\text{RCOOH} : \text{SnCl}_4 = 2$, and belongs to the complexes $\text{RCOOH} \cdot \text{TiCl}_4$ and $2\text{RCOOH} \cdot \text{SnCl}_4$ (structure¹⁰ *Ia*). The second absorption band in the region at about 3300cm^{-1} appears in the excess of TiCl_4 and SnCl_4 over the above mentioned ratios. Its intensity increases on

TABLE III
Vibrations $\nu(\text{O—H})$ of Acid Monomers and of Complexes

Acid	$\nu(\text{O—H}), \text{cm}^{-1}$			Dissociation constant ^b
	DCB ^a	benzene	<i>p</i> -xylene	
CF_3COOH	3 430	3 375	3 350	$5.9 \cdot 10^{-1}$
CCl_3COOH	3 430	3 380	3 350	$1.2 \cdot 10^{-1}$
CF_2HCOOH	3 450	3 410	3 375	$5.7 \cdot 10^{-2}$
CCl_2HCOOH	3 450	3 410	3 375	$5.1 \cdot 10^{-2}$
CH_3COOH	3 495	3 460	3 430	$1.75 \cdot 10^{-5}$
$\text{CH}_3\text{COOH} \cdot \text{SnCl}_4$	3 140 ^c	3 140, 3 330 ^d	3 100, 3 300 ^d	—
$\text{CH}_3\text{COOH} \cdot \text{TiCl}_4$	3 150, 3 260 ^d	3 150, 3 290 ^d	3 150, 3 280 ^d	—
$\text{CCl}_2\text{HCOOH} \cdot \text{TiCl}_4$		3 080	—	—

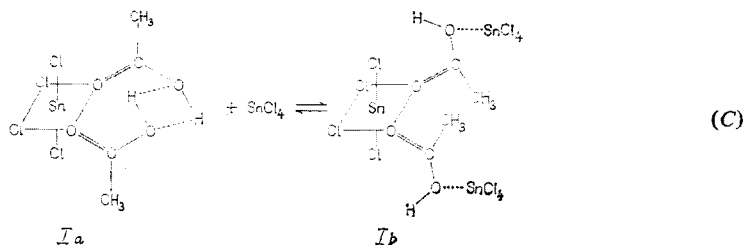
^a 1,2-Dichlorobenzene; ^b ref.²⁰, in water at 25°C; ^c broad shoulder 3 140—3 400 cm^{-1} ; ^d appears at $\text{SnCl}_4/\text{RCOOH} > 0.5$ and $\text{TiCl}_4/\text{RCOOH} > 1$.

the expenses of the intensity of the 3150 cm^{-1} band proportionally with the increasing excess of the Lewis acid and also with the increasing basicity of the aromatic solvent. In the systems with SnCl_4 this band shifts with increasing basicity of the solvent towards lower wavenumbers, similarly as the $\nu(\text{O}-\text{H})$ band of monomer acids. However, in the systems with TiCl_4 the position of this band stays within the limits $3280-3290\text{ cm}^{-1}$, independent of the solvent basicity. The appearance of the $\nu(\text{O}-\text{H})$ band of the higher wavenumber is accompanied by an increase of the bands of the $\nu(\text{C}=\text{O})$ vibrations which are shifted in the TiCl_4 systems by about 20 cm^{-1} towards lower wavenumbers, in SnCl_4 systems by about 20 cm^{-1} towards higher wavenumbers, in comparison with the $\nu(\text{C}=\text{O})$ vibration bands of the respective complexes.

In the systems TiCl_4 -halogenated acetic acids the acids are converted mostly to carboxylate, and together with the complex there remains free acid and TiCl_4 in the solutions. The maximum of the $\nu(\text{O}-\text{H})$ band of the complex cannot be determined, as there is both a band of the acid dimer and of the solvent itself superimposed over it. Neither a large excess of TiCl_4 causes an increase of the absorption bands in the region above 3100 cm^{-1} in the systems with CF_3COOH , CCl_3COOH , CF_2HCOOH , and CCl_2HCOOH . In the system with CCl_2HCOOH an almost total conversion of the acid was reached in the five-fold excess of TiCl_4 , and the $\nu(\text{O}-\text{H})$ band was found at 3080 cm^{-1} .

More accurate positions of the $\nu(\text{O}-\text{H})$ bands were determined using more concentrated (up to 5M) solutions in benzene and deuteriobenzene. It was found also that in all systems with TiCl_4 a fast $\text{H}-\text{D}$ exchange occurred in C_6D_6 . In the system $\text{TiCl}_4-\text{CH}_3\text{COOH}$ the $\nu(\text{O}-\text{D})$ bands were found at 2360 cm^{-1} and 2460 cm^{-1} , in the system CCl_2HCOOH they were at 2300 cm^{-1} ; this corresponds to the frequency ratio $\nu(\text{O}-\text{H})/\nu(\text{O}-\text{D}) = 1.33$. Both the lower wavenumber of the $\nu(\text{O}-\text{H})$ band of the complex $\text{CCl}_2\text{HCOOH} \cdot \text{TiCl}_4$ (3080 cm^{-1}) and the higher rate of the $\text{H}-\text{D}$ exchange show that the complex is more acidic than the complex $\text{CH}_3\text{COOH} \cdot \text{TiCl}_4$ ($\nu(\text{O}-\text{H}) = 3150\text{ cm}^{-1}$). Both systems are much more acidic than the corresponding carboxylic acids, as can be inferred from the large difference in the wavenumbers of the $\nu(\text{O}-\text{H})$ vibrations and in the $\text{H}-\text{D}$ exchange rates. In the system $\text{SnCl}_4-\text{CH}_3\text{COOH}$ in C_6D_6 no $\text{H}-\text{D}$ exchange was observed: this indicates a much lower acidity of this complex in comparison with $\text{CH}_3\text{COOH}-\text{TiCl}_4$. The absorption band of the $\nu(\text{O}-\text{H})$ vibration of the complex $\text{SnCl}_4 \cdot 2\text{CH}_3\text{COOH}$ at 3140 cm^{-1} thus cannot belong to the carboxyl group of the monomer, but rather to the intra-molecular hydrogen bond between the carboxyls in the complex of *Ia* structure. In the excess of SnCl_4 then presumably dissociations of the hydrogen bonds occur due to the solvation by SnCl_4 (equation (C)), and the $\text{O}-\text{H}$ bond vibration appears at 3300 cm^{-1} . The dissociation of the complex *Ia* to *Ib* probably weakens the electron-donor bond $\text{C}=\text{O}$ with SnCl_4 , and this is reflected in the increase of the $\nu(\text{C}=\text{O})$ vibration wavenumber of the complex *Ib* by 20 cm^{-1} . The complex *Ib* shows also a normal behaviour

of the $\nu(\text{O—H})$ vibration of monomeric acids, as its wavenumber in *p*-xylene is by 30 cm^{-1} lower than in benzene.



The complex $\text{TiCl}_4 \cdot \text{CH}_3\text{COOH}$, considerably more acidic, exists presumably only in the monomeric form. The evident decrease of the $\nu(\text{C=O})$ wavenumber in the excess of TiCl_4 can be explained by a further, though weak coordination of TiCl_4 , obviously to the oxygen of the bond C—O—H . The complex thus solvated by TiCl_4 exhibits also an increased wavenumber of the $\nu(\text{O—H})$ vibration; this increase, however, is not dependent on the basicity of the aromatic component. We assume that the solvating molecule TiCl_4 sterically hinders the solvation interaction of the carboxylic hydrogen with the aromatic molecule. Also, the formation of a charge-transfer complex between the solvating TiCl_4 and the aromatic molecule in the vicinity of the carboxyl group may play a role. The aromatic molecule which acts in the charge-transfer complex as an electron donor has a lower π -electron density and, therefore, a lower tendency to solvate the hydrogen of the carboxyl. Stannic chloride as a weaker electron-acceptor forms much weaker complexes with aromatic compounds²¹ and this may be why it does not prevent the solvation of the carboxylic hydrogen in the complex *Ib* by aromatic solvents.

PMR SPECTRA

In the PMR spectra of solutions of CF_3COOH , CCl_3COOH , CH_3COOH , and $(\text{CH}_3)_3\text{CCOOH}$ in benzene as well as in the spectra of catalytic systems the position of the resonant band of the carboxyl group proton was mainly investigated. In a given solvent it depends on the degree of the acid dimer-to-monomer dissociation, and with the increasing concentration of the monomer it shifts to a higher magnetic field^{22,23}. In the PMR spectra of acids solutions a single, narrow resonance band of the carboxylic proton appears as a consequence of both fast exchange of protons between molecules of the acid, and of acid molecules between the dimer and the monomer. The change of the acid concentration from 3 M to 1 M inducing further dissociation of the dimer to the monomer resulted in the proton band shift by 0.70 p.p.m. in CF_3COOH , and

by 0.77 p.p.m. in CCl_3COOH towards a higher magnetic field. In CH_3COOH practically no shift was observed. The shift towards higher magnetic fields is caused by the solvation effect of benzene on the monomer which results in a higher screening of the proton. The curve of the concentration dependence of the proton band position in CF_3COOH lies by 0.75 p.p.m. higher than the corresponding curve of CCl_3COOH . However, this effect cannot be ascribed solely to a stronger interaction of the more acidic proton in CF_3COOH with benzene, because — as observed in the infrared spectra — in a solution of the same concentration CF_3COOH is more dissociated to the monomer than CCl_3COOH .

Titanium tetrachloride-carboxylic acids. In the systems TiCl_4 -carboxylic acids only one band of the carboxylic proton can be observed, too. The systems TiCl_4 with CF_3COOH or CCl_3COOH contain both the dimer and the monomer of the acid as well as the complex $\text{TiCl}_4\cdot\text{RCOOH}$, as shown by the infrared spectra. The proton band half-width is about 40 cps in these systems even at a very low concentration of TiCl_4 . This effect could be explained by an exchange of acidic complex protons with protons of benzene²⁴ (even though no significant change in the band-width of the benzene protons was observed), rather than by a slow exchange between

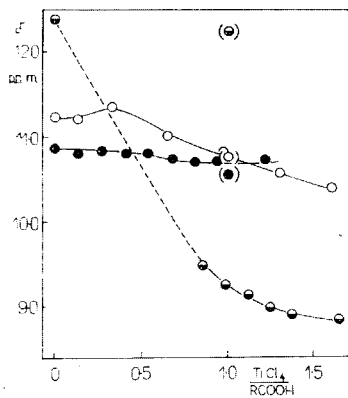


FIG. 2

Dependence of the Chemical Shift δ (p.p.m.) on the Molar Ratio $\text{TiCl}_4:\text{RCOOH}$ in Benzene

○ $\text{R} = \text{CH}_3$, ○ $\text{R} = \text{CCl}_3$, ● $\text{R} = \text{CF}_3$. Points in parentheses indicate the carboxyl proton band position in the acid solution to which the same volume of benzene was added instead of TiCl_4 . Initial concentration $[\text{RCOOH}]_0 = 4.5\text{M}$.

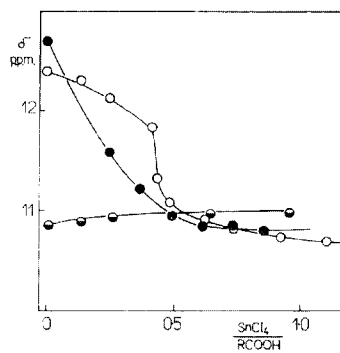


FIG. 3

Dependence of the Chemical Shift δ (p.p.m.) on the Molar Ratio $\text{SnCl}_4:\text{RCOOH}$ in Benzene

○ $\text{R} = \text{CH}_3$, ● $\text{R} = \text{C}(\text{CH}_3)_3$, ● $\text{R} = \text{CF}_3$. Initial concentration $[\text{RCOOH}]_0 = 4.5\text{M}$.

the free acid and the complex. The position of the band of the carboxylic proton shifts in the systems $\text{TiCl}_4\text{-RCOOH}$ with the increasing ratio $\text{TiCl}_4/\text{RCOOH}$ towards a higher magnetic field. However, the magnitude of this shift depends on the nature of system (Fig. 2). The shift of CF_3COOH proton band induced by adding TiCl_4 is somewhat smaller than of the acid diluted by the same volume of benzene instead of TiCl_4 . The infrared analysis shows that only a small amount of the complex is formed in the system, and the small band shift can be explained by diluting benzene with titanium tetrachloride and by the formation of carboxylate (Table I); this results in diminishing the solvation effect of benzene. In the system $\text{TiCl}_4\text{-CCl}_3\text{COOH}$ the effects of benzene dilution are compensated by an increased amount of the complex which causes the band to shift towards a higher magnetic field. The system $\text{TiCl}_4\text{-CH}_3\text{COOH}$ was measured only for molar ratios $\text{TiCl}_4 : \text{CH}_3\text{COOH} \geq 0.9$ when it is homogeneous. A considerable shift of the carboxylic proton band (halfwidth only 4 s.p.s.) towards a higher magnetic field corresponds to a complete transformation of the free acid to the complex $\text{TiCl}_4\cdot\text{CH}_3\text{COOH}$ and to the carboxylate $\text{CH}_3\text{COOTiCl}_3$, observed also by the infrared spectroscopy. A decrease of the complex proton solvation due to benzene in an excess of TiCl_4 , observed in the infrared spectra, was not observed in the PMR spectra. However, as the screening effect of the solvating TiCl_4 is not known and the position of the proton band is influenced by numerous, mutually dependent factors, no detailed conclusions can be made from the PMR spectra.

Stannic tetrachloride-carboxylic acids. Fig. 3 shows the change in the chemical shift of the carboxylic proton with the molar ratio $\text{SnCl}_4/\text{RCOOH}$. In the system with CF_3COOH one can see only a slight band shift towards a lower magnetic field with the increasing content of SnCl_4 . According to the infrared measurement and also according to the published data¹⁰ no interaction between CF_3COOH and SnCl_4 occurs and the slight change in the band position is due to the dilution of the system by SnCl_4 which diminishes the solvation effect of benzene.

In the systems with acetic and pivalic acid an addition of SnCl_4 leads to a considerable shift of the acidic proton band towards a higher magnetic field. In the case of acetic acid the dependence of the band shift on the molar ratio of the components exhibits a clear inflex at $\text{SnCl}_4 : \text{CH}_3\text{COOH} = 0.42$. A somewhat different dependence in the systems with both acids can be explained by the almost an order-of-magnitude higher equilibrium constant for the complex formation with pivalic acid (Table II). The half-widths of the carboxylic protons do not change with the SnCl_4 addition in all these systems. It follows from a considerable shift of the proton bands towards a higher magnetic field that the acetic acid dimer reacts with SnCl_4 to form the assumed complex *Ia*. According to the infrared spectra, this complex then gives in an excess of SnCl_4 the complex *Ib* solvated by SnCl_4 with mutually non-interacting free O—H bonds.

Thus, the PMR spectra of the catalytic systems TiCl_4 , SnCl_4 -carboxylic acids provide a proof of the existence of acidic complexes in these systems, as well as of the monomer structure of carboxylic groups.

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