

794. *Indicator Measurements and Hydrogen Isotope Exchange in the Solvent Systems $\text{SnCl}_4\text{-CH}_3\cdot\text{CO}_2\text{H}$ and $\text{SnCl}_4\text{-HCl-CH}_3\cdot\text{CO}_2\text{H}$.*

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The ionisation of basic indicators in the systems mentioned in the Title for stannic chloride concentrations below *ca.* 3M is described. The rate of aromatic hydrogen isotope exchange has also been measured. Taken together, the results imply that the acidity exhibited is of the Brønsted-Lowry variety.

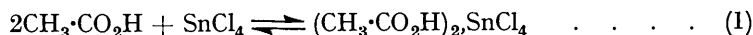
The complex acid $\text{H}_2\text{SnCl}_4(\text{OAc})_2$, which is the active species in the $\text{SnCl}_4\text{-CH}_3\cdot\text{CO}_2\text{H}$ system, is of comparable strength with sulphuric acid. In the presence of hydrogen chloride additional complex formation occurs. The acidic properties of the two systems are compared with those of the analogous systems containing zinc chloride.

THE acidity exhibited by systems containing both Lewis and Brønsted acids has only once been quantitatively studied,¹ namely in solutions of zinc chloride, and zinc chloride and hydrogen chloride, in acetic acid. The present work deals with stannic chloride and hydrogen chloride solutions in the same solvent. As before, the nature of the acidity has

¹ Bethell, Gold, and Satchell, *J.*, 1958, 1918.

been examined with the aid of basic indicators and the aromatic hydrogen isotope exchange reaction.^{1,2}

Stannic chloride dissolved easily in acetic acid, with the evolution of heat, and mole fractions up to *ca.* 0.4 can be obtained. Thereafter the system forms two layers.³ There is no evidence of solvolysis, but good reason⁴ for believing that a complex of composition (CH₃·CO₂H)₂·SnCl₄ is formed between the two components, according to the equilibrium



This is the logical complex to expect, involving as it does six-fold co-ordination. This compound is thought to behave as a complex Brønsted acid,⁴ and appears to be more or less quantitatively solvated by a further molecule of acetic acid, giving the complex (CH₃·CO₂H)₃·SnCl₄ whose solutions possess marked electrical conductivity.^{3,4} The position of the equilibrium (1) therefore seems to be far to the right.

These findings are in keeping with those for solutions of zinc chloride. For these a similar complex, (CH₃·CO₂H)₂·ZnCl₂, is considered to exist. (The usual co-ordination number of zinc is four.) It has been shown to behave as a weak Brønsted acid, and to emphasise this property the formula can be written as H₂ZnCl₂(OAc)₂. Since stannic chloride is a much stronger Lewis acid than is zinc chloride, the complex between the former compound and acetic acid should be much more acidic than H₂ZnCl₂(OAc)₂. The solvent molecules are doubtless complexed *via* the carbonyl oxygen atom, and with the more powerful electrophil stannic chloride there will be a greater drain on the electrons of the oxygen-hydrogen bond, *i.e.*, the ion [SnCl₄(OAc)₂]²⁻ is likely to be more stable than [ZnCl₂(OAc)₂]²⁻.

The expectation of greater strength for the complex acid of tin is clearly confirmed by the apparently quantitative formation of the compound (CH₃·CO₂H)₃·SnCl₄, for this seems to imply the complete ionisation of one proton of H₂SnCl₄(OAc)₂. The marked conductivity also implies appreciable dissociation of the ion pair [CH₃·CO₂H₂]⁺[HSnCl₄(OAc)₂]⁻. The strength of the complex stannic acid is estimated from the experiments now to be described.

Indicator Ionisation.—(i) SnCl₄-CH₃·CO₂H solvent system. The ionisation of five of the indicators usual in acidity-function studies,⁵ namely, *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, *p*-nitrodiphenylamine, and 2:4-dichloro-6-nitroaniline, was investigated. These indicators are negligibly ionised in the pure, anhydrous solvent.¹ As increasing amounts of stannic chloride are added to a solution of one of these compounds in acetic acid, the ultraviolet absorption spectrum gradually changes from that characteristic of the basic form of the indicator to that characteristic of the acidic, or ionised, form, as produced by typical Brønsted acids like sulphuric. Measurement of indicator ionisation ratios, *I* (= ratio of the concentration of ionised to un-ionised form), at various stannic chloride concentrations is thus possible.

The presence of the complex Brønsted acid being assumed, part, at least, of the change in ionisation must be due to it. However, the spectra of the indicators involved are also affected by the addition of small quantities of stannic chloride to their solutions in solvents, such as hexane, with which the stannic chloride will have little chance of forming complexes, and in which, therefore, free Lewis acid will exist. Hence any free stannic chloride which existed in acetic acid would also presumably affect the indicators. To be reasonably sure that the ionisation ratios only reflect the enhanced Brønsted acidity it is necessary to show that, for instance, the rate of some reaction which can only be catalysed by Brønsted acids parallels the changes in ionisation in the way expected. Aromatic hydrogen isotope exchange is a reaction whose rate is usually linear with the extent of ionisation of indicator

² Satchell, *J.*, 1958, 1927.

³ Stranathan and Strong, *J. Phys. Chem.*, 1927, **31**, 1420.

⁴ Usanovich and Kalabanovskaya, *Zhur. obshchei Khim.*, 1947, **17**, 1235.

⁵ Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

bases.⁶ In the present instance the rates of exchange between *p*-deuteroanisole and the solvent systems have been measured. The experiments are described subsequently. The results imply that the ionisation ratios, in fact, reflect only a Brønsted acidity.

The ionisation data for the indicators, at various stannic chloride concentrations, are collected in Table 1. Their main points of interest are the following. (a) The general

TABLE 1. Ionisation of (a) *p*-nitroaniline, (b) *o*-nitroaniline, (c) 4-chloro-2-nitroaniline (d) *p*-nitrodiphenylamine, and (e) 2:4-dichloro-6-nitroaniline in solutions of stannic chloride in acetic acid at $23 \pm 2^\circ$.

SnCl ₄ (M)	0.000035	0.00007	0.00014	0.00028	0.00054	0.00089	0.00178	
log I _a	-1.02	-0.69	-0.16	0.26	0.62	0.87	1.27	
log I _b	—	—	—	-1.44	-1.09	-0.79	-0.44	
log I _b - log I _a	—	—	—	-1.70	-1.71	-1.66	-1.71	
SnCl ₄ (M)	0.00356	0.00534	0.00890	0.0160	0.0267			
log I _b	-0.07	0.26	0.58	1.00	—			
log I _c	-1.05	-0.72	-0.42	-0.03	0.30			
log I _c - log I _b	-0.98	-0.98	-1.00	-1.03	—			
SnCl ₄ (M)	0.0445	0.0710	0.0889	0.142				
log I _a	0.54	0.83	0.95	1.23				
log I _d	-1.01	-0.71	-0.60	-0.33				
log I _d - log I _c	-1.55	-1.54	-1.55	-1.56				
SnCl ₄ (M)	0.231	0.356	0.712	0.856	1.14	1.43	2.14	2.86
log I _d	-0.08	0.16	0.53	0.85	—	—	—	—
log I _e	-1.17	-0.92	-0.55	-0.25	-0.19	0.34	0.56	1.17
log I _e - log I _d	-1.09	-1.08	-1.08	-1.10	—	—	—	—

increase in ionisation with stannic chloride concentration is very similar in form to that observed when hydrogen chloride,⁷ sulphuric acid,⁸ or zinc chloride¹ is added to acetic acid. Fig. 2 shows the data for 4-chloro-2-nitroaniline. (b) For hydrogen chloride,⁷ sulphuric acid,^{5,8} and zinc chloride¹ solutions in acetic acid, the plots of log *I* against the acid concentration for different indicators give curves with fairly constant separations. For any two indicators the exact separations may depend on the acid involved. The separations are also often different from those found when the solvent is water. These discrepancies imply different relative basicities for the indicators under different conditions.^{7,9,10}

In the SnCl₄-CH₃·CO₂H system indicators show similar behaviour to that just described. Table 1 shows that plots of log *I* against stannic chloride concentration would show reasonably constant separations. If the separations be taken to represent the relative basicities of the indicators⁷ then Δ*pK*_a between *p*-nitroaniline and *o*-nitroaniline, between *o*-nitroaniline and 4-chloro-2-nitroaniline, between 4-chloro-2-nitroaniline and *p*-nitrodiphenylamine, and between *p*-nitrodiphenylamine and 2:4-dichloro-6-nitroaniline are -1.70, -1.00, -1.55, and -1.09 respectively. The values for water are -1.28, -0.74, -1.45, and 0.84 respectively.⁵ Such discrepancies are now becoming a commonplace and emphasise the dependence of relative basicity on medium. For zinc chloride in acetic acid¹ Δ*pK*_a for the first three of the above pairs are -1.66, -0.95, and -1.22 respectively; the relative basicities seem, in each case, a little greater in the SnCl₄-CH₃·CO₂H system. (c) In Fig. 1 plots of the ionisation of 4-chloro-2-nitroaniline for various zinc chloride, stannic chloride, hydrogen chloride, and sulphuric acid concentrations in acetic acid are compared. Whereas at the same concentrations zinc chloride produces a much less acidic system than does hydrogen chloride, stannic chloride produces an effect comparable with, or greater than, that produced by sulphuric acid. The acid strength of H₂SnCl₄(OAc)₂ must therefore be considered comparable with that of sulphuric

⁶ Satchell, *J.*, 1956, 3911; and references therein.

⁷ Satchell, *J.*, 1958, 1915.

⁸ Paul and Hammett, *J. Amer. Chem. Soc.*, 1936, 58, 2182; Gold and Hawes, *J.*, 1951, 2102.

⁹ Roček, *Chem. Listy*, 1956, 50, 726.

¹⁰ Satchell, *J.*, 1957, 3524.

acid, though in systems like these relative acidity depends to some extent on the base involved. Since previous experiments^{3,4} probably indicate that one molecule of solvent

TABLE 2. Ionisation of (a) 4-chloro-2-nitroaniline and (b) *p*-nitrodiphenylamine in acetic acid containing both hydrogen chloride and stannic chloride at 23° ± 2°.

(i) HCl (M) = 0.0115								
SnCl ₄ (M)	0.0017	0.0033	0.0049	0.0066	0.0083	0.0149	0.033	0.066
log I _a	-0.36	-0.02	0.15	0.24	0.37	0.52	0.91	1.21
(ii) HCl (M) = 0.115								
SnCl ₄ (M)	0.0083	0.0149	0.042	0.083	0.165	0.346	0.692	1.38
log I _b	-0.74	-0.53	-0.35	-0.05	0.22	0.43	0.71	1.18

is associated with each molecule of H₂SnCl₄(OAc)₂, it is reasonable to assume the complete ionisation of one proton. By analogy sulphuric acid must also be fairly completely ionised in acetic acid.

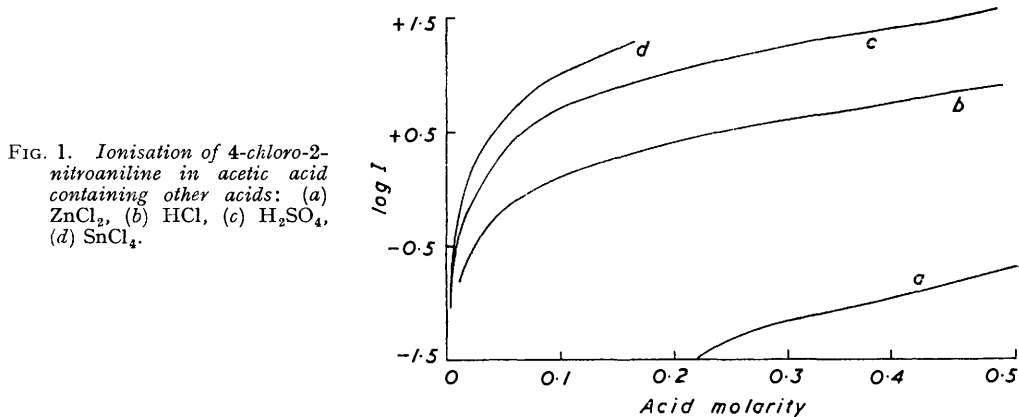


FIG. 1. Ionisation of 4-chloro-2-nitroaniline in acetic acid containing other acids: (a) ZnCl₂, (b) HCl, (c) H₂SO₄, (d) SnCl₄.

(ii) SnCl₄-HCl-CH₃·CO₂H solvent system. Two series of measurements were made also of the change in indicator ionisation when increasing quantities of stannic chloride were added to acetic acid containing a constant amount of hydrogen chloride. The first at 0.0115M-hydrogen chloride used 4-chloro-2-nitroaniline and the second at 0.115M-hydrogen chloride used *p*-nitrodiphenylamine (Table 2). A plot of the results obtained at 0.0115M is given in Fig. 2 where log I is compared with those obtained with the same indicator in the absence of hydrogen chloride.

A definite increase in acidity is found in the presence of hydrogen chloride, but the marked effects found in the ZnCl₂-HCl-CH₃·CO₂H system¹ are absent. In the latter system the acidity increases much more for a given hydrogen chloride concentration, and also passes through a maximum value as the zinc chloride concentration is increased. In explanation two further complex Brønsted acids, besides H₂ZnCl₂(OAc)₂, have been suggested, namely H₂ZnCl₄ and H₂ZnCl₃(OAc). Of these three species, H₂ZnCl₄ is much the most powerful acid. Its initial formation and subsequent replacement by H₂ZnCl₃(OAc) as the zinc chloride concentration becomes large explains the marked increase in acidity and the acidity maximum.

It was hardly possible to predict whether exactly the same effects would be exhibited by the SnCl₄-HCl-CH₃·CO₂H system. Fig. 2 reveals that, in fact, they are not. However, it seems very likely that hydrogen chloride and stannic chloride will combine in suitable solvents, though a medium capable of solvation is probably required. As previously mentioned the favoured co-ordination number is likely to be six. For the SnCl₄-HCl-CH₃·CO₂H system there are, therefore, as for the zinc chloride system, two obvious possibilities besides H₂SnCl₄(OAc)₂, namely H₂SnCl₆ and H₂SnCl₅(OAc).

Fig. 2 reveals that though acidity increases when hydrogen chloride is present (an increase much greater than that to be expected were the hydrogen chloride and stannic chloride to operate independently, so that additional complex formation must be assumed), yet it does not reach a maximum as the stannic chloride concentration rises. The explanation lies, very probably, in the greater strength of $\text{H}_2\text{SnCl}_4(\text{OAc})_2$ than of $\text{H}_2\text{ZnCl}_2(\text{OAc})_2$.

When stannic chloride is added in deficit to hydrogen chloride in acetic acid, the species H_2SnCl_6 is probably preferentially formed. As more stannic chloride is added two possibilities exist. Either the formation of H_2SnCl_6 will be completed, followed by the formation of $\text{H}_2\text{SnCl}_4(\text{OAc})_2$, or the initial H_2SnCl_6 may be replaced by $\text{H}_2\text{SnCl}_5(\text{OAc})$, this being followed by the production of $\text{H}_2\text{SnCl}_4(\text{OAc})_2$. (The effects will, of course, be of the mass-law type, and will not be as sharply distinct as implied in the preceding sentence.) In either case (and the present experiments cannot decide between them,

FIG. 2. Ionisation of 4-chloro-2-nitroaniline in the $\text{SnCl}_4\text{-HCl-CH}_3\text{-CO}_2\text{H}$ solvent system: (\square) $[\text{HCl}] = 0.0115\text{M}$, (\triangle) without HCl.

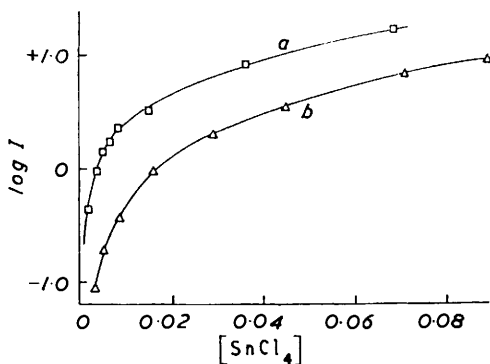
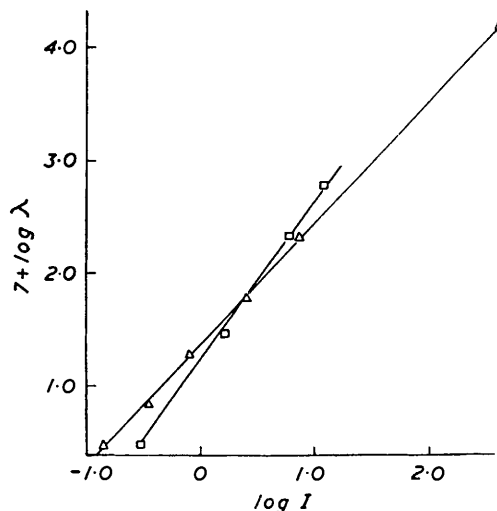


FIG. 3. Aromatic hydrogen isotope exchange in the $\text{SnCl}_4\text{-HCl-CH}_3\text{-CO}_2\text{H}$ solvent system: (\square) $[\text{HCl}] = 0.0115\text{M}$, (\triangle) without HCl.



though the latter scheme seems the more likely) the difference in acidity between H_2SnCl_6 and the other species is likely to be very much less than for the corresponding zinc compounds, for, as we have seen, $\text{H}_2\text{SnCl}_4(\text{OAc})_2$ is itself highly ionised. Thus it is quite understandable that no maximum should be exhibited in the presence of hydrogen chloride, for even if H_2SnCl_6 is replaced by $\text{H}_2\text{SnCl}_5(\text{OAc})$ as stannic chloride is added, it is probable that the loss of acidity involved will be more than compensated by the $\text{H}_2\text{SnCl}_4(\text{OAc})_2$ which must also simultaneously be formed.

Hydrogen isotope exchange reaction. To demonstrate that the observed ionisation ratios were really reflecting only the Brønsted, and not also the Lewis, acidity of the systems, the rate of hydrogen isotope exchange between *p*-deuteroaniline and the various media was studied. This reaction must reflect primarily the Brønsted acidity. For systems which possess only this type of acidity, a large body of previous work^{6,11} shows that a plot of the logarithm of the first-order exchange rate constant (λ) against $\log I$ customarily provides a straight line with a slope close to unity. (A slope of *ca.* 1.15 appears usual for anisole.⁶)

The exchange data are collected in Tables 3 and 4. In Fig. 3 $\log \lambda$ is plotted against $\log I$ for *p*-nitrodiphenylamine. The graph for the solutions of stannic chloride alone is

¹¹ Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309.

an excellent straight line of slope 1.12. The plot in the presence of hydrogen chloride has a greater slope, *viz.*, 1.40. This is in keeping with the results for the $\text{ZnCl}_2\text{-HCl-CH}_3\cdot\text{CO}_2\text{H}$ system, where the exchange rate also increases somewhat more rapidly than the indicator ionisation demands.² When more than one acidic species is active in the solvent such behaviour is to be expected, since under such conditions the ionisation ratios for different

TABLE 3. Hydrogen isotope exchange between *p*-deuteroanisole and the $\text{SnCl}_4\text{-CH}_3\cdot\text{CO}_2\text{H}$ system at 25°.

SnCl_4 (M)	0.059	0.118	0.22	0.596	0.879	2.90
$10^7\lambda$ (sec. ⁻¹) ...	3.01	7.10	19.5	63.1	211	15,900
$\log I$ *	-0.85	-0.45	-0.10	0.40	0.86 †	2.30 †

* For *p*-nitrodiphenylamine.

† Extrapolated values, the data for 2 : 4-dichloro-6-nitroaniline being borne in mind.

TABLE 4. Hydrogen isotope exchange between *p*-deuteroanisole and the $\text{SnCl}_4\text{-HCl-CH}_3\cdot\text{CO}_2\text{H}$ system at 25° ([HCl] = 0.115M).

0.015	0.147	0.732	1.10
3.05	29.8	225	617
-0.53	0.20	0.78	1.27

bases are unlikely to run particularly parallel, and relative basicities are unlikely to remain constant.⁷ The fact that the plot obtained in the presence of hydrogen chloride crosses that obtained with stannic chloride alone is reasonably to be attributed to this cause.

Any free stannic chloride in solution, while it would increase indicator ionisation, would form a complex also with the anisole, and in so doing probably deactivate the ring, and so decrease the exchange rate. Thus, were any free stannic chloride actually present, the observed parallelisms between isotope exchange rate and indicator ionisation seem unlikely to exist. If straight lines were observed, they would have slopes less than unity. Further the ultraviolet absorption spectrum of anisole in the $\text{SnCl}_4\text{-CH}_3\cdot\text{CO}_2\text{H}$ system provides no evidence of complex formation. Altogether, therefore, it seems likely that little free stannic chloride is present in solutions in acetic acid (at any rate below 3M) and that indicator ionisation reflects only a Brønsted acidity.

EXPERIMENTAL

Materials.—Anhydrous acetic acid, m. p. >16.6°, was prepared as previously described.⁶ The indicators were recrystallised samples. Baker "Analysed" stannic chloride was used for most experiments. Hydrogen chloride was that supplied in lecture bottles by Matheson Co. Inc. *p*-Deuteroanisole was a sample from previous work.⁶ Ordinary anisole was redistilled, b. p. 154°.

Ionisation Measurements.—These were made by standard techniques⁷ with a Beckman spectrophotometer at 23° ± 2°. All solutions except those of *p*-nitroaniline were reasonably stable. A small extrapolation to zero time was used for *p*-nitroaniline.

Ultraviolet Spectrum of Anisole.—Usanovich and Pichugina's experiments with mixtures of anisole and stannic chloride show that a dissociating complex is formed which is bright yellow.¹² Experiments with anisole in solutions of stannic chloride in dichloroacetic acid (in which free stannic chloride is present) also indicate a coloured complex. The ultraviolet spectrum of anisole in the present $\text{SnCl}_4\text{-CH}_3\cdot\text{CO}_2\text{H}$ systems reveals no absorption at wavelengths >3000 Å. There can thus be negligible complex formation.

Exchange Experiments.—These were measured under homogeneous conditions at 25° by methods analogous to those previously described.⁶ Anisole was stable in the solutions used.

Reliability of the Measurements.—The similarity between the shapes of the ionisation curves in the presence and the absence of hydrogen chloride and the large effect of small quantities of this compound make it difficult to be sure that some of the acidity exhibited by the, supposedly hydrogen chloride-free, stannic chloride solutions is not, in fact, due to either a small amount of solvolysis or a trace of hydrogen chloride in the stannic chloride. However, the spectra were stable with time, the exchange rates provided good first-order plots, and the

¹² Usanovich and Pichugina, *Zhur. obshechi Khim.*, 1956, **26**, 2415.

addition of small quantities of water reduced the observed acidity. All these facts argue against solvolysis. Further, a specimen of stannic chloride, vacuum-distilled at room temperature with the collection of a middle cut (a procedure which should have removed at least some of any dissolved hydrogen chloride) showed no decrease in acidity.

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