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ACIDITY OF $Cl_3SnCH_2CH_2CO_2H$

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Summary

Interaction of $Cl_3SnCH_2CH_2CO_2H$ with aniline bases in CH_2Cl_2 solution has been studied by UV-visible spectroscopy. As measured by the extents of complexation with the bases, $Cl_3SnCH_2CH_2CO_2H$ is a stronger acid than the corresponding esters, $Cl_3SnCH_2CH_2CO_2R$ (Lewis acids) and also very much more stronger than the Brønsted acid, $CH_3CH_2CO_2H$. The enhanced Brønsted acidity arises from the stabilisation of the anion, $Cl_3SnCH_2CH_2CO_2^-$, by the intramolecular coordination of the tin centre by the carboxylate group.

Introduction

Combinations of Lewis acids and proton acids have found considerable use as catalysts in cationic oligomerizations and polymerizations [1,2] as well as in Friedel–Crafts reactions [3]. These co-acid or dual-acid mixtures have considerably greater acidity than the proton acid component alone. Interactions of the acid partners may lead to an irreversible reaction (e.g. as with $AlCl_3$ or $TiCl_4$ with carboxylic acids, RCO_2H) or to stable adducts (e.g. as with $SnCl_4/RCO_2H$ systems). Tin tetrahalide/carboxylic acid combinations have proved particularly amenable for study. Formation of $SnCl_4 \cdot 2RCO_2H$ complexes (I) in solution has been indicated by IR studies, with complexation occurring via the carbonyl group of the carboxylic acid [4,5]. Furthermore, measures of the acidity of complexes I, acting as monobasic acids, were gained from protonation of aniline bases in aprotic solutions [6], eq. 1.

$$\underset{\text{(I)}}{[SnCl_4 \cdot 2RCO_2H]} + ArNH_2 \rightleftharpoons \underset{\text{(II)}}{\{[ArNH_3]^+\ [SnCl_4 \cdot RCO_2H \cdot RCO_2]^-\}} \qquad (1)$$

The organotin chloride, $Cl_3SnCH_2CH_2CO_2H$ (III), possesses both features of a co-catalyst system and so could act as (i) a Lewis acid having a similar acidity to

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other organotin trichlorides, such as $BuSnCl_3$ [7] or more significantly to $Cl_3SnCH_2CH_2CO_2R$ (IV, R = Me, Et, etc.) [8], (ii) a Brønsted acid, having a similar acidity to $CH_3CH_2CO_2H$, and/or (iii) an intramolecular dual-acid, having an appreciably greater acidity than $CH_3CH_2CO_2H$.

In this paper, we report our findings on the acidity of III.

Experimental

The compound, $Cl_3SnCH_2CH_2CO_2H$ (III) was prepared from $SnCl_2$, HCl and $CH_2{=}CHCO_2H$ [9]; it was recrystallised from dry CH_2Cl_2/petroleum ether; m.p. 123–125 °C (lit. [9] m.p. 123–127 °C). Analysis. Found: C, 12.2; H, 1.5; Cl, 35.3. $C_3H_5Cl_3O_2Sn$ calcd.: C, 12.1; H, 1.7; Cl, 35.7%. ^1H NMR (220 MHz, $CDCl_3$) δ 11.25 (s(br), 1H, OH), 3.08 (t, 2H, $SnCH_2$), 2.20 (t, 2H, CH_2CO) ppm. ^{13}C NMR (20 MHz, CD_3COCD_3): δ 185.08 (CO), 29.20 ($SnCH_2$), 28.55 (CH_2CO) ppm.

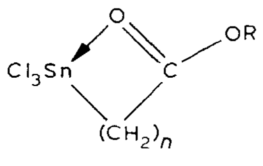
Dichloromethane was dried over CaH_2 and distilled prior to use. Aniline bases were redistilled or recrystallised commercial samples. Propionic acid, dichloroacetic acid and trifluoroacetic acid were redistilled commercial samples.

Determination of equilibrium constants

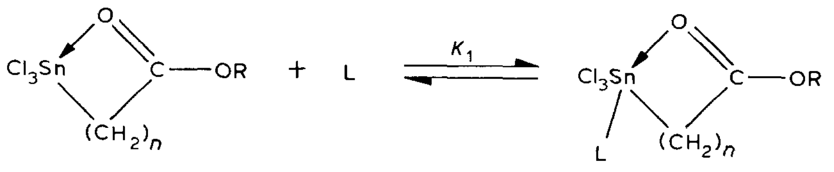
Equilibrium constants were determined from UV-visible spectral data obtained at 25 ± 1 °C in CH_2Cl_2 solution. Solutions were made-up and optical cells filled within a dry-box. Absorptions were measured at suitable wavelengths (usually λ_{max} of the aniline) for a number of solutions containing different concentrations of III or the carboxylic acid with a constant concentration of an aniline base (ca. 10^{-4} M). The equilibrium constants were calculated from the absorptions using standard equations [8,10]. For the carboxylic acid–aniline interactions, there were progressive but slight shifts in λ_{max} of the uncomplexed aniline to shorter wavelengths on addition of the carboxylic acid to the CH_2Cl_2 solutions. For these solutions, absorptions at λ_{max} were used to calculate the equilibrium constants.

Results and discussion

The acid III and the ester derivatives IV have similar structures. IR spectra show that III and IV [8,9,11,12] are chelated species containing 5-coordinate tin both in the solid state and in solution. A similar situation was found for $Cl_3Sn(CH_2)_3CO_2Et$ (V) [13]. The ν(C=O) values in CH_2Cl_2 solution for III, IV (R = Et), V and $CH_3CH_2CO_2Et$ (1645, 1668, 1663 and 1740 cm^{-1}) clearly point to the coordination



(III, R = H, n = 2;
IV, R = Me, Et, etc, n = 2;
V, R = Et, n = 3)



(2)

(VI)

(IV, $n = 2$ or V, $n = 3$)

(L = RNH_2, Py etc.; $K_1 = [VI] / [Cl_3Sn(CH_2)_nCO_2R][L]$)

of the carbonyl groups. Confirmation of the solid state chelated structures has come from X-ray structure determination studies for IV (R = Me) [12], IV (R = Pr^i) [14] and V [13]. The esters IV are thus ideal Lewis acid standards with which to compare the acidity of the acid III. The Lewis acidities or acceptor strengths of IV (R = Me) [8], IV (R = Et) [13] and V [13] towards monodenate nitrogen donors, e.g. Py and anilines, have previously been found to be markedly similar from the values of formation constants in CH_2Cl_2 solution (Table 1 and eq. 2). The ligand, L, coordinates to tin without breakage of the carbonyl–tin complexation and so gives rise to the hexa-coordinate compounds VI, e.g. ν(C=O) in CH_2Cl_2 for VI ($n = 3$, R = Et, L = Py) is 1648 cm^{-1} [13].

The acidity of III in this study was also investigated in CH_2Cl_2 solution at 25 ± 1°C by UV-visible spectroscopy using aniline bases, $PhNH_2$, p-$ClC_6H_4NH_2$, m-$ClC_6H_4NH_2$ and 4-Me-3-$NO_2C_6H_3NH_2$; in addition, interaction of the carboxylic acids, $CH_3CH_2CO_2H$, $CHCl_2CO_2H$ and CF_3CO_2H were also studied using similar conditions. All the aniline interactions, whether involving the Lewis acids IV or V [8,13], the carboxylic acids or III, led to similar spectral changes, namely loss of the longest wavelength absorption of the aniline (see e.g. Fig. 1) without generation of any long wavelength charge-transfer absorption, as noted for some $SnCl_4$ interactions [15]. However, additions of the reactive proton acids caused progressive, but slight, shifts of λ_{max} of the free anilines to shorter wavelengths. It has been stated

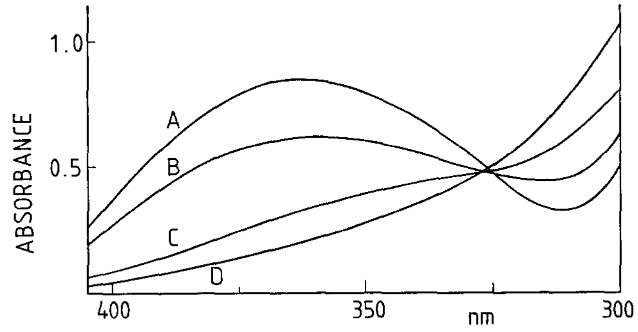


Fig. 1. Interaction of $Cl_3SnCH_2CH_2CO_2H$ and 4-Me-3-$NO_2C_6H_3NH_2$ in CH_2Cl_2 solution at 25 ± 1° C. [4-Me-3-$NO_2C_6H_3NH_2$] 1×10^{-4} M; [$Cl_3SnCH_2CH_2CO_2H$] 0 (A); 8.66×10^{-3} M (B) 34.6×10^{-3} M (C); 69.2×10^{-3} M (D).

that there can be problems associated with the measurement of acidity constants for proton acid/base systems in non-aqueous media [16,17]. In aprotic solvents, such as PhH, CCl_4 or CH_2Cl_2, there is certainly a different acidity (or basicity scale) for every reference base (or acid) used, and not the single acidity scale as found in H_2O. Relative strengths of carboxylic acids towards amine bases, including $BuNH_2$ and $PhNEt_2$ [18] have been obtained in PhH [19] and in $CHCl_3$ [18] solution, using values of the association constants (K_2) of the stable hydrogen-bonded ion-paired 1/1 adducts VII (eq. 3).

$$RNH_2 + R'CO_2H \overset{K_2}{\rightleftharpoons} \underset{\text{(VII)}}{\{[RNH_3]^+ [R'CO_2]^-\}} \qquad (3)$$

$$(K_2 = [\text{VII}]/[RNH_2][R'CO_2H])$$

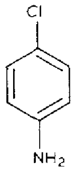
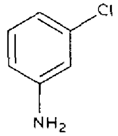
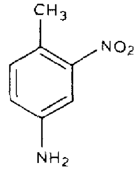
Sequences of acid strengths of carboxylic acids in such solvents follow sequences in H_2O, e.g. K_a (at 25 °C in H_2O) [K_2, towards $BuNH_2$ in $CHCl_3$ solution] values are $10^{-4.87}$ [$10^{2.45}$], $10^{-1.29}$ [$10^{6.2}$] and $10^{-0.23}$ [$10^{7.7}$] for $CH_3CH_2CO_2H$, $CHCl_2CO_2H$ and CF_3CO_2H, respectively.

The absorption data for III–$ArNH_2$ systems in CH_2Cl_2 were also satisfactorily analyzed in terms of ion-paired 1/1 adducts (eq. 4), with dissociation into free ions

TABLE 1

VALUES OF log (formation constants) OF 1/1 ADDUCTS OF $Cl_3Sn(CH_2)_nCO_2R$ WITH ANILINE BASES IN CH_2Cl_2 SOLUTION AT 25 °C

$Cl_3Sn(CH_2)_nCO_2R + ArNH_2 \rightleftharpoons [(ArNH_2)Cl_3Sn(CH_2)_nCO_2R]$

Aniline	pK_a [a]	log (formation constants)			
		$Cl_3Sn(CH_2)_2$-CO_2H [b]	$Cl_3Sn(CH_2)_2$-CO_2Me [c]	$Cl_3Sn(CH_2)_2$-CO_2Et [d]	$Cl_3Sn(CH_2)_3$-CO_2Et [d]
$PhNH_2$	4.60	2.90 ± 0.1	1.50 ± 0.1	1.52 ± 0.1	1.48 ± 0.1
	3.98	2.45 ± 0.1			
	3.52	1.95 ± 0.1			
	3.02	1.54 ± 0.1			

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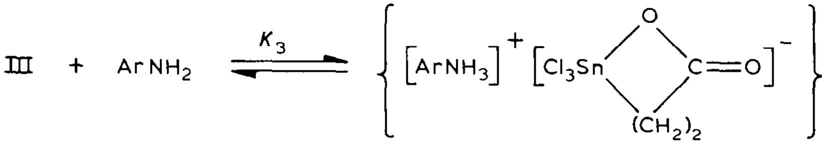
[a] In H_2O at 25 °C. [b] This study. [c] Ref. 8. [d] Ref. 13.

being ignored (dielectric constant of CH_2Cl_2 is 9.08 at 20 °C). Values of K_3 are listed in Table 1.



(4)

(VIII)

$$(K_3 = [\mathrm{VIII}] \, / \, [\mathrm{III}] \, [ArNH_2]$$

Unfortunately values of K_2 for RCO_2H–aniline interactions in CH_2Cl_2 were not obtained with any great accuracy (Table 2), one problem being the shift in λ_{max} of the aniline on addition of the carboxylic acid. The values in Table 2 have not been corrected for the dimerisation of these acids; values of the dimerisation constants in CH_2Cl_2 solution are not known, although they are in other aprotic solvents (see e.g. ref. 20 and 21).

From the values of the formation constants of adducts of III, IV, V and RCO_2H with aniline it can be concluded that III is (i) more acidic than IV (R = Me or Et) and V by a factor of approximately 25, and (ii) considerably more acidic than $CH_3CH_2CO_2H$ (by a factor of approximately 10^3) and is comparable in acidity to CF_3CO_2H in CH_2Cl_2 solution. Any inductive effect of the Cl_3Sn group on the ionization of the CO_2H group can only be small and the large enhancement in acidity must result from another effect, namely the internal complexation within III or more significantly within the anion of III.

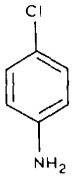
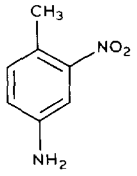
Solutions of anilines and III are not stable for long periods. The instability is more pronounced the more basic is the aniline. We feel that this is due to the base-catalysed formation of $[Cl_2Sn^+CH_2CH_2CO_2^-]$. A compound having the em-

TABLE 2

VALUES OF $\log K_2$ FOR THE 1/1 INTERACTION OF CARBOXYLIC ACIDS WITH ANILINES IN CH_2Cl_2 SOLUTION AT 25 °C

$$RCO_2H + ArNH_2 \overset{K_2}{\rightleftharpoons} \{[ArNH_3]^+[RCO_2]^-\}$$

$$K_2 = \{[ArNH_3]^+[RCO_2]\}/[RCO_2H][ArNH_2]$$

	log K_3		
	PhNH₂		
$CH_3CH_2CO_2H$	−0.3 ± 0.1		
$CHCl_2CO_2H$		1.5 ± 0.1	0.65 ± 0.1
CF_3CO_2H			1.5 ± 0.1

pirical formula $C_3H_4Cl_2O_2Sn$ has been previously recognised as a readily obtainable product from III, e.g. on refluxing III in xylene solution [9].

One factor controlling the acid-strength of dual-acid systems must be the acceptor strength of the Lewis acid part. Alkyltin trichlorides are much weaker Lewis acids than $SnCl_4$ [7] and so the dual acidity of III should be less than that of $RCO_2H/SnCl_4$ combinations. This showed in the necessity to use much more basic aniline bases with III than used previously with $RCO_2H/SnCl_4$ combinations [6].

There is a correlation, eq. 5, between the pK_a values of $ArNH_2$ in H_2O at 25 °C and log K_3 values for interactions of $ArNH_2$ with III in CH_2Cl_2 solutions at 25 °C.

$$pK_a = 1.15 + 1.18 \log K_3 \tag{5}$$

From previous work on the acidity of I, a log K_4 value of 1.9 is deduced for the protonation of *o*-nitrodiphenylamine ($pK_a = -2.96$) by $[SnCl_4 \cdot 2CH_3CH_2CO_2H]$ (I, R = CH_3CH_2) in *o*-dichlorobenzene solution at 25 °C (eq. 6) [6]. From eq. 5 log K_3

$$\underset{(\mathrm{R}=\mathrm{CH_3CH_2})}{\mathrm{I}} + \underset{(\mathrm{IX})}{\mathrm{PhNHC_6H_4NO_2}\text{-}o} \overset{K_4}{\rightleftharpoons} \left\{\underset{(\mathrm{X})}{[\mathrm{PhNH_2C_6H_4NO_2}\text{-}o]^+[\mathrm{SnCl_4 \cdot RCO_2H \cdot RCO_2}]^-}\right\} \tag{6}$$

$$(K_4 = [\mathrm{X}(\mathrm{R} = \mathrm{CH_3CH_2})]/[\mathrm{IX}][\mathrm{I}(\mathrm{R} = \mathrm{CH_3CH_2})])$$

for interaction of III with a base of pK_a −2.96, is calculated to be −3.5. Ignoring differences in solvents, it appears that I (R = CH_3CH_2) is $> 10^5$ times more acidic than III.

References

1 P.H Plesch, The Chemistry of Cationic Polymerisation, Pergamon Press, New York, 1963.
2 Y. Imanishi, S. Kohjiva, and S. Okamura, J. Macromol. Sci. (Chem.) A2, (1968) 471
3 G.A Olah (Ed.) Friedel–Crafts and Related Reactions. Interscience, London, Vol. 1, 1963.
4 D.P.N. Satchell and J.L. Wardell, Trans. Faraday Soc., 61 (1965) 1132.
5 K. Mach and E. Drahoradova, Coll. Czech. Chem. Commun., 40, (1975) 326
6 D.P.N. Satchell and J.L. Wardell, Trans. Faraday Soc., 61 (1965) 1127.
7 J.L. Wardell, J. Organomet. Chem., 9 (1967) 89.
8 D. Maughan, J.L Wardell, and J.W. Burley, J. Organomet. Chem., 212 (1981) 59.
9 R.E. Hutton, J.W. Burley, and V. Oakes, J. Organomet. Chem., 156 (1978) 369.
10 J.L Wardell, J Chem. Soc A, (1971) 2628
11 R.M. Haigh, A G. Davies, and M.-W. Tse, J. Organomet. Chem., 174 (1979) 163.
12 P J. Harrison, T.G. King, and M.A Healy, J. Organomet. Chem., 182 (1979) 7.
13 R.A. Howie, E.S. Paterson, J.L Wardell, and J.W Burley, J Organomet. Chem., 259 (1983) 71.
14 R.A. Howie, E.S. Paterson, J.L. Wardell, and J.W. Burley, to be published
15 D.P.N Satchell and J.L. Wardell, J. Chem. Soc., (1964) 4134.
16 E.J. King, Acid-Base Equilibria, Pergamon Press, Oxford 1965.
17 R.P. Bell, Proton in Chemistry, 2nd edition, Chapman–Hall, London, 1973.
18 M. Rumeau and B. Tremillon, Bull. Soc. Chim. France, (1964) 1049, M Rumeau, Ann. Chim. (Paris), 8 (1971) 131.
19 M.M. Davis and M. Raabo, J. Org. Chem., 31 (1966) 1804 and earlier papers.
20 D P.N. Satchell and J.L. Wardell, Trans. Faraday Soc., 61 (1965) 1199
21 I.S. Perelygin, A.M. Afanas'eva, and A.K. Khairetdinova, J Struct. Chem, Engl. Transl., 19 (1978) 648; S.D. Christian and T.L. Stevens, J. Phys. Chem., 76 (1972) 2039.