

Note

Measurement of the Hydrolysis of Tin Tetraacetate by Proton and Carbon-13 NMR Spectroscopy

Hann-Jenn Lin^{*a} (林漢鎮), Yun-Huin Lin^b (林昀輝),
Jyh-Horung Chen^{*b} (陳志鴻) and Lian-Pin Hwang^c (黃良平)

^aDepartment of Chemical Engineering, National I-Lan Institute of Agriculture and Technology,
I-Lan 26051, Taiwan, R.O.C.

^bDepartment of Chemistry, National Chung Hsing University, Taichung 40227, Taiwan, R.O.C.

^cDepartment of Chemistry, National Taiwan University and Institute of Atomic and Molecular Sciences,
Academia Sinica, Taipei 10764, Taiwan, R.O.C.

Solid-state ¹³C CP/MAS spectral analysis of the hydrolysis products of Sn(OAc)₄ allowed the hydrolysis intermediates, Sn(OH)(OAc)₃, Sn(OH)₂(OAc)₂ and Sn(OH)₃(OAc), to be identified. The results show that the hydrolysis consists of three steps; the first and second steps are consecutive reactions and the third is reversible. Intermolecular exchange between hydrolysis products (i.e. Sn(OAc)₄, Sn(OH)(OAc)₃, Sn(OH)₂(OAc)₂ and Sn(OH)₃(OAc)) and acetic acid was observed from the measurement of ¹H and ¹³C solution spectra at varied temperatures in CD₂Cl₂ with $\Delta G_{248}^{\ddagger}$ 50.5 kJ mol⁻¹.

INTRODUCTION

Tin tetraacetate, Sn(OAc)₄, is described as an eight-coordinate structure with four bidentate acetate groups around each tin atom.¹ The ¹³C NMR spectrum of Sn(OAc)₄ dissolved in CDCl₃ at 25 °C shows single signals for both the carbonyl (184.75 ppm) and the methyl (18.07 ppm) carbon atoms.² The methyl ¹H NMR signals of Sn(OAc)₄ in CDCl₃ is reported at 2.22 ppm at 25 °C by Straughan et al.² and 2.05 ppm at 33 °C by Alcock et al.³ Samples used for previous measurement of NMR spectra of ¹H and ¹³C nuclei likely contained acetic acid as a result of hydrolysis. The discrepancy in the chemical shift of the methyl protons may reflect the extremely hygroscopic nature of the compound.

We examined the proton and ¹³C NMR spectra of Sn(OAc)₄ in CD₂Cl₂ solution at low temperatures to observe whether there is intermolecular exchange among the tin-containing hydrolysis products and acetic acid. Solid state ¹³C CP/MAS NMR spectra of Sn(OAc)₄ were measured to detect the various hydrolysis products.

EXPERIMENTAL SECTION

Preparation of Sn(OAc)₄ Solution

Sn(OAc)₄ (from Aldrich) was dissolved in CD₂Cl₂ (99.6% from Aldrich) at a concentration 9.86×10^{-2} M for

the NMR measurements.

Preparation of Tin-Containing Mixture by Reacting of Sn(OAc)₄ with Excess Water

H₂O (10 mL) was added to a solution of Sn(OAc)₄ (70.9 mg) in (25 mL) of CHCl₃. The mixture was shaken overnight. After the solvent CHCl₃ and H₂O were removed on a rotary evaporator, white crystals resulted. These crystals were dried in vacuo at 80 °C to remove water and HOAc. The final crystals dissolved in neither water nor organic solvents such as CHCl₃, CH₂Cl₂, CH₃OH and C₆H₆. Elemental analysis indicated C 11.0% and H 2.8%. In accordance with these data, the elemental ratio of C and H was about 1 to 3. Hence a mixture with Sn(OH)₃(OAc) as a predominant component resulted when Sn(OAc)₄ was reacted with excess water.

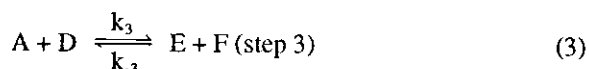
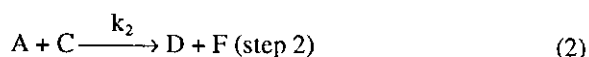
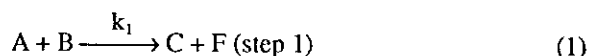
NMR Spectra

¹H and ¹³C NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, on a spectrometer (Bruker AM-400) in dichloromethane-d₂, locked on solvent deuterium, and referenced internally to TMS. The temperature of the spectrometer probe was calibrated by the shift difference of the methanol signal in the ¹H NMR spectrum. CP/MAS ¹³C solid-state NMR spectra were recorded at 26 °C on 50.33 MHz, using a solid-state NMR spectrometer (Bruker MSL-200). Dry nitrogen gas was used to drive MAS rates of 3-4

KHz. Analytical data of remaining compounds are presented in the succeeding section.

RESULTS AND DISCUSSION

The hydrolysis of $\text{Sn}(\text{OAc})_4$ is expressed as a three-step reaction. Let $A = \text{H}_2\text{O}$, $B = \text{Sn}(\text{OAc})_4$, $C = \text{Sn}(\text{OH})(\text{OAc})_3$, $D = \text{Sn}(\text{OH})_2(\text{OAc})_2$, $E = \text{Sn}(\text{OH})_3(\text{OAc})$ and $F = \text{HOAc}$. The hydrolysis of B is expressed as



in which k_1 and k_2 are the rate constants of steps 1 and 2 respectively; k_3 and k_{-3} are the rate constants of the forward and reverse process in step 3. The principle of material balance yields

$$[B] + [C] + [D] + [E] = [B]_0 + [C]_0 + [D]_0 + [E]_0 \quad (4)$$

in which the subscript 0 denotes the initial concentration of the respective chemical species.

A high-resolution solid-state ^{13}C NMR spectrum of B was recorded just after the sample was opened to ambient air. As shown in Fig. 1(I) and Table 1, B absorbed traces of water and hydrolysis occurred immediately after opening. Four methyl carbon signals appeared: B 17.2 ppm (0.15), C 18.2 ppm (0.19), D and F 20.9 ppm (0.07), E 23.9 ppm (0.59), and three carbonyl carbon signals: B and C 187.2 ppm, E 181.0 ppm, D and F 176.2 ppm; the relative intensities are given in parentheses. Hence hydrolysis proceeded according to Eqs. (1)-(3). Without sample spinning, the solid ^{13}C CP-NMR spectrum of B showed two sharp lines, due to the liquid acetic acid HOAc as a result of hydrolysis with carbonyl carbon signals at 177.2 ppm and methyl carbon signal at 21.1 ppm. The carbon signals of HOAc merged with those of carbonyl and methyl carbons of D at 26 °C. After exposure of B to the atmosphere for one week, further water was absorbed and the ^{13}C spectrum and corresponding chemical shifts and intensities of the solid state are in Fig. 1(II) and Table 1 for the intermediate case. As the water concentration increased, the relative intensities of B and C decreased from 0.15 and 0.19 to trace amount, respectively, whereas those of D and E increased from 0.07 to 0.10 and from 0.59 to 0.88, respectively. The solid-state ^{13}C

CP/MAS spectrum and data of crystals obtained from the hydrolysis of B with excess water are presented in Fig. 1(III) and Table 1, respectively. The signal of the methyl carbon in B and C completely disappeared, shown in Fig. 1(III), indicating that Eqs. (1) and (2) were irreversible reac-

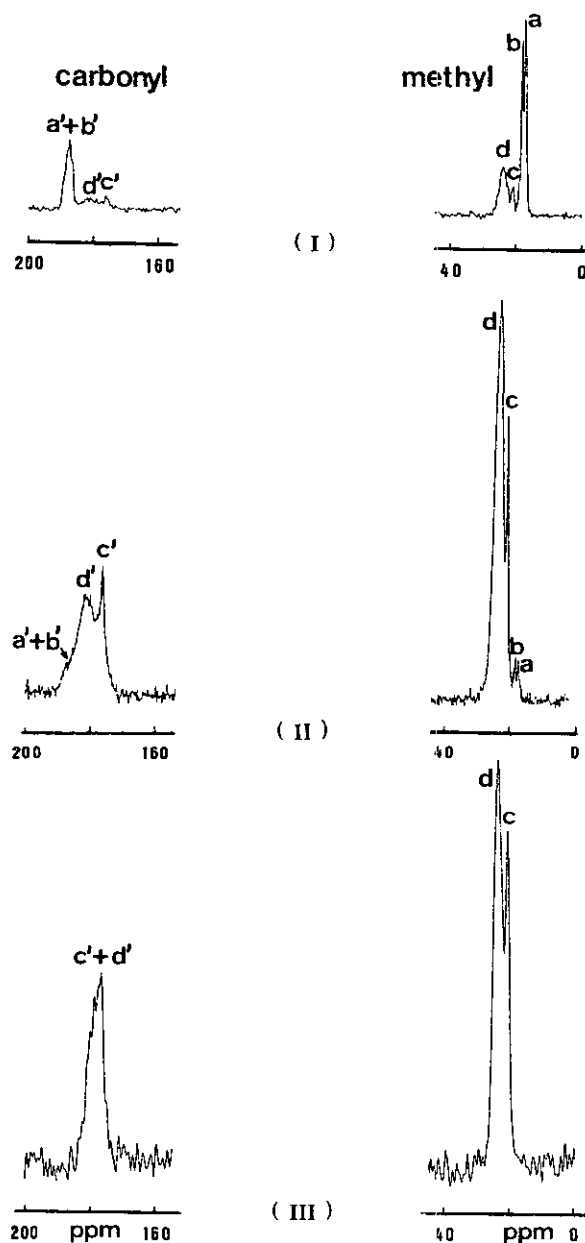


Fig. 1. Solid-state ^{13}C CP/MAS spectra of $\text{Sn}(\text{OAc})_4$ at 26 °C with a trace of water (I), an intermediate amount (II) and excess (III). The carbon assignments are methyl carbons of (a) $\text{Sn}(\text{OAc})_4$, (b) $\text{Sn}(\text{OH})(\text{OAc})_3$, (c) $\text{Sn}(\text{OH})_2(\text{OAc})_2 + \text{HOAc}$ and (d) $\text{Sn}(\text{OH})_3(\text{OAc})$ and the carbonyl carbon atoms of (a' + b') $\text{Sn}(\text{OAc})_4 + \text{Sn}(\text{OH})(\text{OAc})_3$, (d') $\text{Sn}(\text{OH})_3(\text{OAc})$ and (c') $\text{Sn}(\text{OH})_2(\text{OAc})_2 + \text{HOAc}$.

Table 1. ^{13}C Chemical Shifts δ/ppm for Solid-State CP/MAS Data of $\text{Sn}(\text{OAc})_4$ at Various of Water Concentrations^a

Amount of water	C^*OCH_3			COC^*H_3			
	$\text{Sn}(\text{OAc})_4$ + $\text{Sn}(\text{OH})(\text{OAc})_3$	$\text{Sn}(\text{OH})_3(\text{OAc})$	$\text{Sn}(\text{OH})_2(\text{OAc})_2$ +HOAc	$\text{Sn}(\text{OH})_3(\text{OAc})$	$\text{Sn}(\text{OH})_2(\text{OAc})_2$ +HOAc	$\text{Sn}(\text{OH})(\text{OAc})_3$	$\text{Sn}(\text{OAc})_4$
Trace	187.2	181.0	176.2	23.9 (0.59)	20.9 (0.07)	18.2 (0.19)	17.2 (0.15)
Intermediate	187.0	181.0	176.1	23.7 (0.88)	21 (0.10)	18.1 (d)	17.3 (d)
Excess	-		177.3 ^b	23.4 (0.83)	20.5 ^c (0.17)	- (0)	- (0)

^a Chemical shift/ppm relative to TMS. Value in parentheses are the relative concentrations normalized according to Eq. (4).

^b Averages of $\text{Sn}(\text{OH})_3(\text{OAc})$ and $\text{Sn}(\text{OH})_2(\text{OAc})_2$ are given.

^c Chemical shift is due to only $\text{Sn}(\text{OH})_2(\text{OAc})_2$.

^d Trace amount.

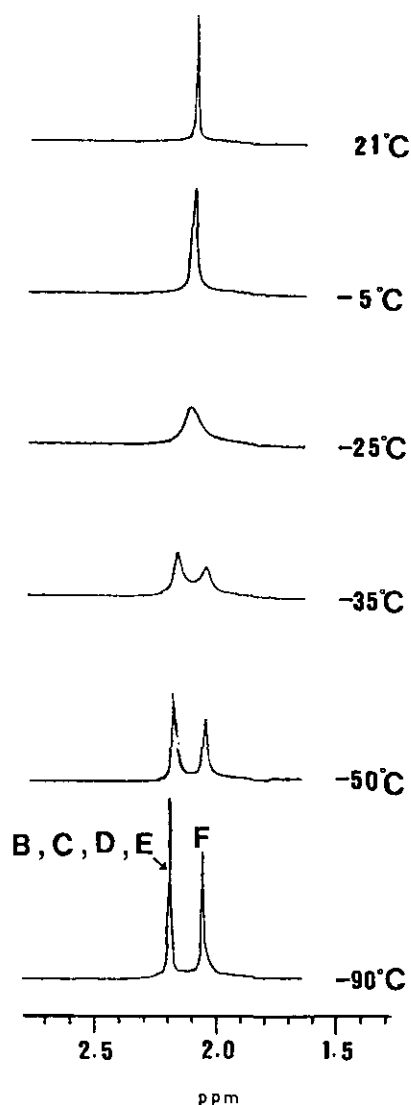


Fig. 2. ^1H NMR spectra (400 MHz) of the acetato protons in $\text{Sn}(\text{OAc})_4$ in CD_2Cl_2 at various temperatures.

tions. That step (3) was reversible was indicated by the relative intensity of E that decreased from 0.88 to 0.83 and whereas of D increased from 0.10 to 0.17. The two-component mixture consisting of 83% E and 17% of D in Fig. 1(III) confirms the elemental analysis data that indicated that E is a major component in the mixture. The singlet of the carbonyl carbon showed similar behavior in Fig. 1(II) and Fig. 1(III).

When a solution 9.86×10^{-2} M of B in CD_2Cl_2 (Fig. 2) was cooled, the methyl proton signal, a single peak at 21°C ($\delta = 2.16$ ppm), first broadened (temperature of coalescence, $T_c = -25^\circ\text{C}$) and then split into two peaks of separation 53.2 Hz. At -90°C , the peak of chemical shift 2.15 ppm corre-

Table 2. ^{13}C Chemical Shifts δ/ppm and Tin-Carbon Coupling Constant J/Hz of $\text{Sn}(\text{OAc})_4$ in CD_2Cl_2 at Varied Temperature^a

Temp./ $^\circ\text{C}$	C^*OCH_3		COC^*H_3	
	A + B + C + D	HOAc	HOAc	A + B + C + D
25	184.8 ^c			18.1 ^c
21	184.0 ^d			18.5 ^d
-57	186.7	179.2	21.6	18.2
-70	186.9	179.5	21.8	18.3
-90	186.9 (65 Hz)	179.6	21.9	18.5 (76 Hz)
21	-	177.3 ^e	21.1 ^c	-

^a Chemical shifts/ppm relative to TMS. Values in parentheses are J ($\text{Sn}-^{13}\text{C}$) coupling constants in Hertz.

^b A = $\text{Sn}(\text{OAc})_4$, B = $\text{Sn}(\text{OH})(\text{OAc})_3$, C = $\text{Sn}(\text{OH})_2(\text{OAc})_2$, D = $\text{Sn}(\text{OH})_3(\text{OAc})$.

^c From Ref. 2.

^d Average chemical shifts are given.

^e Chemical shifts for the pure acetic acid.

sponds to the methyl proton of acetic acid (F); the peak at 2.28 ppm is due to the B, C, D, E; and the signal of the hydroxyl group of HOAc is 12.81 ppm, to be compared with 11.15 ppm at 21 °C. As the process of exchange between B, C, D, E and F is completely reversible, this process is treated as simple two-site exchange; conventional coalescence analysis yields $\Delta G^{\ddagger}_{248}$ 50.5 kJ mol⁻¹.

¹³C NMR spectra and data for B in CD₂Cl₂ at various temperatures appear in Fig. 3 and Table 2, respectively. At -90 °C, because the intermolecular exchanges among B, C,

D, E and F (HOAc) are extremely slow, methyl and carbonyl carbons of the acetato group are observed at 18.5 ppm [³J (Sn-¹³C) = 76 Hz] (and 21.9 ppm) and 186.9 ppm [²J (Sn-¹³C) = 65 Hz] (and 179.6 ppm) for B, C, D, E (and F), respectively. At 21 °C, intermolecular exchange of the acetato group is rapid, indicated by single signals due to both carbonyl (184.0 ppm) and methyl (18.5 ppm) carbon atoms.

The single resonances of the ¹H (methyl proton δ = 2.16 ppm) and ¹³C (carbonyl carbon δ = 184.0 ppm and methyl carbon δ = 18.5 ppm) at 21 °C are explained as due to rapid intermolecular exchange among the tin-containing hydrolysis products and HOAc. The ¹³C CP/MAS spectral analysis at 26 °C allowed us to detect the various hydrolysis products; the result indicates that this hydrolysis is a three-step reaction.

ACKNOWLEDGMENT

We thank the National Research Council of the R.O.C. (Grants NSC 82-0208-M-005-013 and NSC 82-0115-C-005-0021) for support.

Received August 6, 1993.

Key Words

Hydrolysis; NMR of Sn(OAc)₄.

REFERENCES

1. Alcock, N. W.; Tracy, V. L. *Acta Cryst.* **1979**, B35, 80.
2. Straughan, B. P.; Moore, W.; McLaughlin, R. *Spectrochim. Acta* **1986**, 42A, 451.
3. Alcock, N. W.; Tracy, V. L. *J. Chem. Soc., Dalton Trans.* **1976**, 2243.

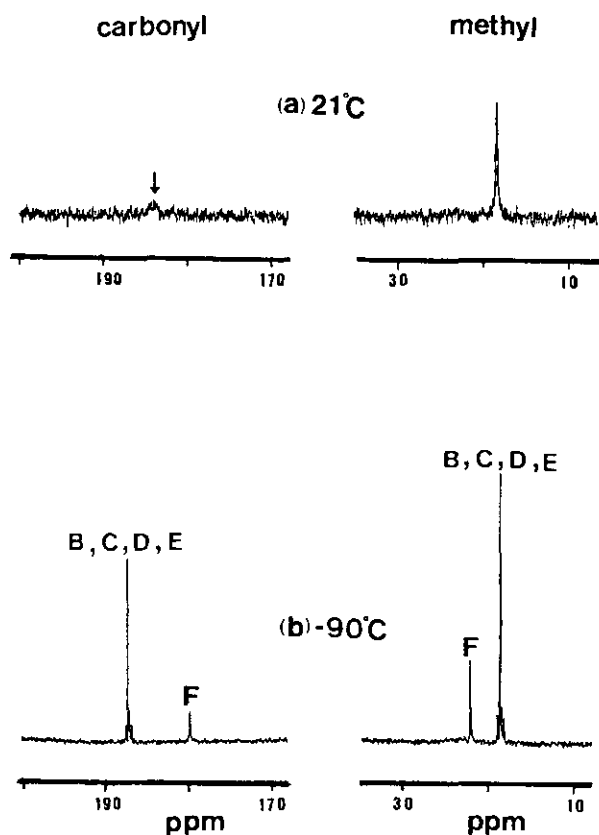


Fig. 3. ¹³C spectra of Sn(OAc)₄ in CD₂Cl₂ at (a) 21 °C; (b) -90 °C.