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Stability Constants of Dimethyltin Dichloride and Tin Tetrachloride Complexes of *p*-Substituted Benzaldehydes, Acetophenones and *N*,*N*-Dimethylbenzamides

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Many stable dimethyltin dichloride - organic donor adducts have been isolated and their configurations in the solid state discussed by several workers.[1] Only a few quantitative data on them[1-3] in solution have been reported, however, although the stability constants of other organotin chlorides[4-7] and tin tetrachloride adducts[8] have been obtained. Recently we have reported that dimethyltin dichloride forms stable 1 : 1 adducts with some aromatic carbonyl donors and that their stability constants are quite small.[1] The present report will describe the stability constants for several dimethyltin dichloride and tin tetrachloride-aromatic carbonyl donor (XC_6H_4COR) complexes and the effect of the substituents, X and R groups.

Experimental

Materials. *N,N*-Dimethylbenzamide and its *p*-substituted derivatives were prepared according to the methods in the literature.[9] *p*-Nitro-*N,N*-dimethylbenzamide. Found: C, 55.90; H, 5.18; N, 14.87%. Calcd for $C_9H_{10}N_2O_3$: C, 55.66; H, 5.19; N, 14.42%. *p*-Chloro-*N,N*-dimethylbenzamide. Found: C, 58.53; H, 5.61; N, 7.84%. Calcd for $C_9H_{10}ClNO$: C, 58.86; H, 5.49; N, 7.62%. *N,N*-Dimethylbenzamide. Found: C, 72.12; H, 7.43; N, 9.41%. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39%. *p*-Methyl-*N,N*-dimethylbenzamide. Found: C, 73.18; H, 7.80; N, 8.64%. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58%. *p*-*N,N*-Dimethylamino-*N,N*-dimethybenzamide. Found: C, 68.42; H, 8.59; N, 14.52%. Calcd for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57%. The *p*-methoxy-*N,N*-dimethylbenzamide, kindly supplied by Professor Komori of this Department, was also analytically pure. The *p*-*N,N*-dimethylacetophenone was prepared according to the literature, and excellent analyses for carbon, hydrogen, and nitrogen were obtained on it.[1] The other acetophenone- and benzaldehyde derivatives were commercially-available materials and were distilled under nitrogen before use. Dimethyltin dichloride and dibromide, tin tetrachloride and 1,2-dichloroethane were purified according to the conventional methods.[3]

Spectrophotometers. The IR and UV spectrophotometers used here were previously described.[1]

Results and Discussion

The stability constants (K) of the complexes are defined by the following equation;

$$K = [A \cdot D]/[A] \cdot [D], \text{ in } A + D = A \cdot D$$

where A is dimethyltin dichloride or tin tetrachloride and where D is a carbonyl donor. The K values were determined from the infrared (Fig. 1) or ultraviolet spectra (Fig. 1 in Ref. 1) for the carbonyl donor molecules with varying amounts of the tin(IV) compounds in 1,2-dichloroethane, according to the method described previously.[1]

The results obtained for the dimethyltin dichloride and tin tetrachloride complexes are summarized in Tables 1 and 2, respectively. Dimethyltin dichloride - carbonyl donor complexes were isolated stably as 1:1 adducts rather than as 1:2 adducts,[1] and under the present experimental conditions a large excess of dimethyltin dichloride exists in

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Table 1. Stability constants (log K) of dimethyltin dichloride - aromatic carbonyl donor complexes in 1,2-dichloroethane at 25±2°C

D	X $(CH_3)_2N$	CH_3O	CH_3	H	Cl	NO_2
$XC_6H_4COCH_3$	$0.50 \pm 0.02^{a,b)}$ $(0.11 \pm 0.03)^{a,c)}$	$0.03 \pm 0.02^{a,b)}$		-0.22 ± 0.08		
XC_6H_4COH	$0.89 \pm 0.02^{a,b)}$	$0.52 \pm 0.10^{a)}$	$0.21 \pm 0.02^{a)}$	-0.19 ± 0.03		
$XC_6H_4CON(CH_3)_2$	1.64 ± 0.03	1.37 ± 0.02	1.45 ± 0.02	1.34 ± 0.02	1.16 ± 0.02	0.86 ± 0.02

a) Determined from UV spectra and the others from IR spectra.
b) Ref. 1.
c) The value of dimethyltin dibromide complex.

Table 2. Stability constants (log K) of tin tetrachloride - aromatic carbonyl donor complexes in 1,2-dichloroethane at 25±2°C

D	X CH_3O	CH_3	H	Cl
$XC_6H_4COCH_3$	2.62 ± 0.02		1.65 ± 0.04	
XC_6H_4COH	3.27 ± 0.02	2.60 ± 0.02	2.16 ± 0.06	1.93 ± 0.03

Determined from UV spectra.

Table 3. C=O stretching frequencies of aromatic carbonyl donors and their frequency lowerings (in parentheses) accompanied by the complex formation with dimethyltin dichloride in 1,2-dichloroethane (in cm^{-1})

D	X $(CH_3)_2N$	CH_3O	H	Cl	NO_2
$XC_6H_4COCH_3$	1665 (24)	1680 (20)	1686 (16)		
XC_6H_4COH	1665 (26)	1688 (24)	1706 (16)		
$XC_6H_4CON(CH_3)_2$	1626 (41)	1630 (36)	1633 (36)	1637 (37)	1643 (29)

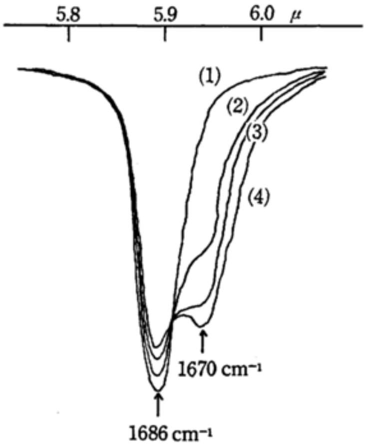

Fig. 1. The infrared spectrum of $C_6H_5COCH_3$ (0.0438 mol/l) with various concentrations of $(CH_3)_2SnCl_2$ in 1,2-dichloroethane.
$(CH_3)_2SnCl_2$: (1) 0, (2) 0.344, (3) 0.728, (4) 1.037 mol/l

solution in comparison with the donors. Therefore, the formation of the 1 : 1 adducts may be predominant in solution. In the cases of tin tetrachloride, the 1 : 2 adducts were isolated stably.[10,11] However, the K values obtained here may also be considered to be those for the 1 : 1 adducts, because of the large excess of tin tetrachloride compared with the donors. Tables 1 and 2 indicate that the acceptor strength of tin chlorides toward carbonyl donors is; $SnCl_4 : (CH_3)_2SnCl_2 \fallingdotseq 500—100 : 1$. Furthermore, we can compare the acceptor strength of the latter toward *N,N*-dimethylbenzamide derivatives with that of iodine studied by Drago:[9] $(CH_3)_2SnCl_2 : I_2 \fallingdotseq 5 : 1$.

Generally, the order of the electron-releasing tendency of R in XC_6H_4COR is known to be $H < CH_3 < N(CH_3)_2$. This is indicated in the C=O

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stretching frequencies of the free ligands (Table 3); the frequency decreases with a stronger electron-releasing group, R or X. Table 3 also shows the C=O frequency shift to a lower region due to the complex-formation with dimethyltin dichloride. The magnitudes of the frequency lowering are compared with the *K* values. The association constants of the substituted acetophenones with protons were reported to be larger than those of substituted benzaldehydes.[12,13] In the cases of tin chloride complexes, however, the *K* value and the C=O frequency lowering become larger in the following order of R groups; $CH_3 < H < N(CH_3)_2$, as may be seen in Tables 1, 2, and 3. This order for H and CH_3 groups may be due to the steric effect of the methyl group on the complex formation of tin chlorides.

There is an almost linear relationship between the $\log K$ and σ^+ values of *p*-substituents, X, in XC_6H_4COR ($R=H$, CH_3 and $N(CH_3)_2$). Similarly, linear relationships of $\log K$ against σ^+ values have been previously mentioned for boron trifluoride complexes of substituted benzamides[14] and for the protonation of substituted acetophenones and benzaldehydes.[12,13]

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