# Addition and Substitution Reactions of Tin(II) Dimethoxide

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Reactions involving addition of M–ER systems (E = O, S, N, P, *etc.*) to multiple bonds are well known in tin(IV) systems,[1] where, for example, organotin(IV) alkoxides add to isocyanates to give *N*-stannylcarbamates.[2] We report the behaviour of the analogous tin(II) dimethoxide, which can be summarized in three general equations:

$$\mathrm{Sn(OR^1)_2 + A{=}B \rightarrow Sn(A{\cdot}B{\cdot}OR^1)_2}\ \textit{or}\ \mathrm{Sn(B{\cdot}A{\cdot}OR^1)_2} \tag{1}$$

$$\mathrm{+\ 2R^2EH \rightarrow Sn(ER^2)_2 + 2R^1OH} \tag{2}$$

$$\mathrm{+\ 2R^2EX \rightarrow SnX_2 + 2R^2EOR^1} \tag{3}$$

for which we present examples. Tin(II) dimethoxide was prepared by the method of Haendler, *et al.*,[3] and used immediately.

Phenyl isocyanate undergoes a highly exothermic reaction with $Sn(OMe)_2$ in petrol to give in virtually quantitative yield a white solid whose i.r. spectrum exhibits strong absorptions at 1730 [$\nu$(C=O)], 1070 and 1083 cm.$^{-1}$ [$\nu$(C–O)]. Hydrolysis gave methyl *N*-phenylcarbamate, consistent with the formulation of the product as bis(methyl *N*-phenylcarbamate)tin(II), m.p. (sealed tube) 109—114°. The $^{119m}$Sn Mössbauer spectrum, run immediately, exhibited a doublet with isomer shift consistent with the formulation as tin(II).[4] Phenyl isothiocyanate was allowed to react slowly with $Sn(OMe)_2$ at room temperature to give an oil whose i.r. spectrum contained a strong absorption at 1140 cm.$^{-1}$, which can be assigned to $\nu$(C=S) in a more unambiguous manner. In addition, the ready hydrolysis of the product to form methyl *N*-phenylthiocarbamate can be taken as evidence for N–Sn rather than S–Sn bonding by analogy with the relative hydrolytic sensitivities of the tin(IV) systems.[2,5] Chloral reacted exothermically with $Sn(OMe)_2$ to produce in virtually quantitative yield the crystalline tin(II) acetal, $Sn[OCH(CCl_3)OMe]_2$, m.p. (sealed tube) 73—74°, whose i.r. spectrum contained very strong, broad absorptions at 1080 and 830 cm.$^{-1}$ which can be assigned to $\nu$(C–O) and $\nu$(C–Cl) respectively. The Mössbauer spectrum confirmed the presence of tin as tin(II), but the hydrolysis product showed a $\nu$(O–H) absorption at 3390 cm.$^{-1}$ and Mössbauer spectroscopy showed that the tin had been oxidised to $Sn^{IV}$.

Thiophenol reacted with $Sn(OMe)_2$ in benzene according to equation (2) with no evolution of heat. The pale yellow solid, m.p. 158—160° with darkening, formed in virtually quantitative yield, exhibited a doublet Mössbauer spectrum consistent with tin as tin(II), but a resonance in the tin(IV) region slowly appeared. Tin(II) dithiophenoxide takes up thiophenol in refluxing benzene after ½ hr., or on standing in air for 2 days, to give tin(IV) tetrathiophenoxide which is also produced directly from tin(II) dimethoxide and thiophenol in the presence of triethylamine.

Benzoyl chloride reacted with $Sn(OMe)_2$ according to equation (3) in an exothermic reaction to give tin(II) chloride and methyl benzoate in 82% yield.

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