

calculated it with the help of Eq. (6).

$$V_e = \frac{-2.5C + [(2.5C)^2 - 4(10.05C^2)(1-\eta)]^{1/2}}{2(10.05)C^2} \dots (6)$$

$V_e$  has been strictly defined as the volume which a mole of solute particles occupies when considered, from purely hydrodynamic reasons, as rigid microscopic spheres. Since  $B$  coefficient is a measure of ion-solvent interaction, Breslau and Miller<sup>7</sup> have obtained the relationships (7) and (8) for monovalent and bivalent ions:

$$B = 2.90V_e - 0.018 \dots (7)$$

$$B = 6.06V_e - 0.041 \dots (8)$$

In this note an attempt has been made to find a correlation of the  $B$  coefficient obtained from our data<sup>8</sup> by utilizing the Eq. (2) at  $\alpha = 1$  with  $V_e$  for seventeen electrolytes at 10, 20 and 30% (by wt) in dioxane-water mixtures at  $35^\circ \pm 0.005^\circ$ . The values of  $B$  and  $V_e$  thus obtained are recorded in Table 1.

The electrolytes used were of extra pure quality (E. Merck). Experimental technique adopted has been described earlier<sup>1</sup>. The time of flow has an accuracy of  $\pm 0.04$  to  $0.08\%$  and density readings are accurate up to 4 in  $10^6$ .

The plot of  $B$  vs  $V_e$  is found to be linear and the following equations fit the data (both graphically and by least square methods):

$$B = 1.33V_e - 0.020 \quad (\text{in } 10\% \text{ dioxane})$$

$$B = 2.19V_e - 0.033 \quad (\text{in } 20\% \text{ dioxane})$$

$$B = 3.25V_e - 0.100 \quad (\text{in } 30\% \text{ dioxane})$$

This indicates that the slope of the plot of  $B$  versus  $V_e$  changes with the change in the dielectric constant. This can be explained as follows: As a result of solute-solvent interaction small density changes take place at the interface in the solute and the solvent molecules. These density changes lead to changes in the microscopic viscosities of the solvent at the interface. This is reflected either as an increase or decrease in Einstein's slope, depending upon whether the microscopic viscosities are, respectively, higher or lower than the pure

solvent value. As the dielectric constant decreases, the divalent ion as a result of higher charge density, tends to induce much more structuring in the solvent at the interface. This results in an increase in microscopic viscosity of the solvent at the interface.

A gradual increase in viscosity and hence an increase in the  $B$  value is observed as the dioxane content of the solvent medium is increased (Table 1). This phenomenon seems obvious in terms of increasing intermolecular association<sup>9</sup> between water and dioxane with the formation of bigger molecules.

The value of  $V_e$  decreases with the decrease in dioxane content of the solvent, in agreement with the theoretical expectation. This may be interpreted in terms of the bond formation between water and dioxane molecules. As dioxane content is increased more and more hydrogen bonded dioxane-water molecules are formed resulting in an increase in  $V_e$  (Table 1).

The values of  $B$  and  $V_e$  for the same solvent composition and for the same anion are not the same for different cations. The magnitude of  $B$  and  $V_e$  is higher for cations carrying greater charge and hence these are more structure-forming than the ions carrying lower charge which give higher value of  $V_e$ . The order is:  $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ ;  $Zn^{2+} > Ni^{2+} > Mg^{2+}$ ; and  $Na^+ > K^+$ .

#### References

1. DAS, P. K. & PATNAIK, D., *Curr. Sci.*, **25** (1956), 337.
2. DAS, P. B., *J. Inst. Chem.*, **48** (1976), 207.
3. TUAN, D. F. T. & FOUSS, R. M., *J. phys. Chem.*, **67** (1967), 1843.
4. SKINNER, J. F. & FOUSS, R. M., *J. phys. Chem.*, **68** (1964), 2998.
5. EINSTEIN, A., *Annln Phys.*, **19** (1906), 289; **34** (1911), 591.
6. KURUSCEV, T. SARGASSON, A. M. & WEST, B. O., *J. phys. Chem.*, **61** (1957), 1567.
7. BRESLAU, B. & MILLER, I. F., *J. phys. Chem.*, **74** (1970), 1956.
8. DAS, P. B., Ph.D. thesis, Utkal University, 1967.
9. RHODEWALD, P. & MOLDNER, H., *J. phys. Chem.*, **77** (1973), 373.

#### Reactions of Organotin Isopropoxides with Acetyl Pseudohalides

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Reactions of trialkyltin isopropoxides,  $R_3SnOPr^i$  (where  $R = Et, Pr^n$  or  $Bu^n$ ) and dialkyltin diisopropoxides,  $R_2Sn(OPr^i)_2$  (where  $R = Me, Et$  or  $Bu^n$ ) with acetyl pseudohalides,  $CH_3COX$  (where  $X = CN$  or  $NCS$ ) give compounds of the types  $R_3SnX$ ,  $R_2Sn(OPr^i)(X)$  and  $R_2Sn(X)_2$ . The compounds have been characterized on the basis of molecular weight, infrared spectral and volatility data.

TRIETHYLTIN cyanide is one of the earliest known organometallic pseudohalides<sup>1</sup>. Later on, many more organotin pseudohalides have been

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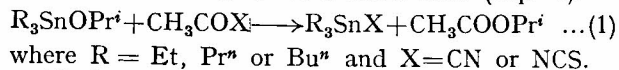
TABLE 1 — VALUES OF  $B$  AND  $V_e$  IN DIFFERENT DIOXANE-WATER MIXTURES (WT %)

Electrolyte	$B$			$V_e$		
	10%	20%	30%	10%	20%	30%
BaCl <sub>2</sub>	0.211	0.364	0.514	0.112	0.152	0.186
SrCl <sub>2</sub>	0.308	0.412	0.512	0.118	0.154	0.199
CaCl <sub>2</sub>	0.276	0.368	0.518	0.128	0.164	0.201
MgCl <sub>2</sub>	0.430	0.458	0.742	0.190	0.244	0.292
BaBr <sub>2</sub>	0.202	0.393	0.534	0.130	0.197	0.286
MgBr <sub>2</sub>	0.356	0.542	0.779	0.191	0.247	0.358
Ba(ClO <sub>4</sub> ) <sub>2</sub>	0.218	0.318	0.495	0.123	0.154	0.226
Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.271	0.412	0.684	0.122	0.210	0.270
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.110	0.280	0.330	0.064	0.122	0.153
Sr(NO <sub>3</sub> ) <sub>2</sub>	0.200	0.270	0.400	0.107	0.128	0.157
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.340	0.390	0.433	0.130	0.156	0.194
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.380	0.420	0.500	0.161	0.195	0.216
Na <sub>2</sub> SO <sub>4</sub>	0.255	0.264	0.313	0.130	0.148	0.156
K <sub>2</sub> SO <sub>4</sub>	0.228	0.238	0.288	0.122	0.138	0.141
MgSO <sub>4</sub>	0.610	0.660	—	0.258	0.269	—
NiSO <sub>4</sub>	0.690	0.710	—	0.292	0.397	—
ZnSO <sub>4</sub>	0.670	0.680	—	0.269	0.287	—

synthesized by different workers using different methods<sup>2-8</sup>.

In view of our earlier work on the synthesis of a variety of alkoxy pseudohalides of a number of metals (Ti, Zr, Nb or Ta) by the straightforward reactions of their alkoxides with acetyl pseudohalides<sup>9,10</sup>, it was thought worth while to investigate the possibility of the synthesis of organotin pseudohalides by similar reactions.

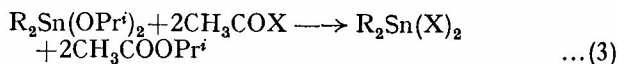
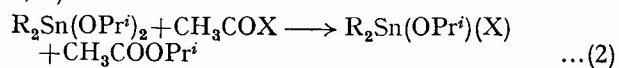
The reactions of trialkyltin isopropoxides, R<sub>3</sub>SnOPr<sup>i</sup> with acetyl pseudohalides have been carried out in equimolar ratios in cyclohexane. The reactions are exothermic and can be completed by refluxing the reaction mixtures for a short time (Eq. 1).



All these trialkyltin cyanides or thiocyanates can be distilled or sublimed under reduced pressure.

Ebullioscopic molecular weight determinations show that triethyl- and tributyl-tin cyanides are initially associated, but the degree of association tends to decrease with continued refluxing and the final molecular weights correspond to the formula weights. The trialkyltin thiocyanates are also monomeric in refluxing benzene.

Similarly dialkyltin diisopropoxides, R<sub>2</sub>Sn(OPr<sup>i</sup>)<sub>2</sub>, react with acetyl pseudohalides in the molar ratios 1:1 and 1:2 to give dialkyltin alkoxy pseudohalides and dialkyltin dipseudohalides respectively (Eqs. 2, 3):



where R = Me, Et or Bu<sup>n</sup>, X = CN or NCS.

These products can also be distilled or sublimed under reduced pressure. Cyanide derivatives of dialkyltin diisopropoxides have a tendency to crystallize out as fine crystals from cyclohexane and these are sparingly soluble in benzene. All the thiocyanato derivatives of dialkyltin diisopropoxides are monomeric in benzene.

The infrared spectra of organotin pseudohalides and alkoxy pseudohalides have been recorded in the range 4000-400 cm<sup>-1</sup> in nujol or in the neat form. All the organotin cyanides and thiocyanates show bands in the region 2200-1950 which have been assigned to the νCN frequencies. Other bands, due to νCS and δNCS frequencies for the thiocyanate group, could not be assigned definitely because of the presence of bands due to organic moiety in the same region.

*Organotin isopropoxides* — The organotin isopropoxides were synthesized by the reactions of the corresponding chlorides with sodium isopropoxide and distilled or sublimed under reduced pressure. The boiling points (in °C/mm) of these organotin isopropoxides synthesized during the course of present investigations were found to be as follows: Et<sub>3</sub>SnOPr<sup>i</sup>, 83-84/12.0; Pr<sub>3</sub>SnOPr<sup>i</sup>, 92-95/4.0; Bu<sub>3</sub>SnOPr<sup>i</sup>, 125/5.0; Me<sub>2</sub>Sn(OPr<sup>i</sup>)<sub>2</sub>, 130-35/6.0 (sublimed); Et<sub>2</sub>Sn(OPr<sup>i</sup>)<sub>2</sub>, 75/3.5; Bu<sub>2</sub>Sn(OPr<sup>i</sup>)<sub>2</sub>, 131-32/10.0.

Acetyl cyanide (Fluka) was used after distillation (b.p. 93°).

TABLE 1 — REACTIONS OF ORGANOTIN ISOPROPOXIDES WITH ACETYL CYANIDE AND ISOTHIOCYANATE

Reactants (g)	Molar ratio	Product (nature)	b.p. °C/mm (yield, %)	Found (Calc.), %		Mol. wt Found (Calc.)
				Sn	N	
Et <sub>3</sub> SnOPr <sup>i</sup> (2.52) + CH <sub>3</sub> COCN (0.66)	1:1	Et <sub>3</sub> SnCN (white solid)	130-35/0.5 (72)*	51.51 (51.22)	5.82 (6.04)	240.0 (231.8)
Et <sub>3</sub> SnOPr <sup>i</sup> (3.22) + CH <sub>3</sub> CONCS (1.23)	1:1	Et <sub>3</sub> SnNCS (yellow liquid)	130/1.0 (80)†	44.96 (44.98)	5.28 (5.35)	260.0 (263.8)
Pr <sub>3</sub> SnOPr <sup>i</sup> (2.76) + CH <sub>3</sub> CONCS (0.91)	1:1	Pr <sub>3</sub> SnNCS (yellow liquid)	160/2.5 (80)*	38.72 (38.84)	4.47 (4.58)	310.0 (305.7)
Bu <sub>3</sub> SnOPr <sup>i</sup> (2.40) + CH <sub>3</sub> COCN (0.47)	1:1	Bu <sub>3</sub> SnCN (colourless low melting solid)	145-50/0.5 (90)†	37.68 (37.56)	4.20 (4.43)	308.0 (316.1)
Bu <sub>3</sub> SnOPr <sup>i</sup> (2.35) + CH <sub>3</sub> CONCS (0.68)	1:1	Bu <sub>3</sub> SnNCS (colourless liquid)	178/1.5 (70)†	34.93 (34.10)	4.23 (4.02)	340.0 (348.11)
Me <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (2.71) + CH <sub>3</sub> CONCS (1.03)	1:1	Me <sub>2</sub> Sn(OPr <sup>i</sup> )(NCS) (white solid)	150-55/1.0 (40)*	44.34 (44.69)	5.03 (5.27)	273.0 (265.7)
Me <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (2.47) + CH <sub>3</sub> CONCS (1.87)	1:2	Me <sub>2</sub> Sn(NCS) <sub>2</sub> (white solid)	175-80/1.0 (50)	44.37 (44.85)	10.33 (10.58)	272.0 (264.7)
Et <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (1.43) + CH <sub>3</sub> COCN (0.67)	1:2	Et <sub>2</sub> Sn(CN) <sub>2</sub> (white solid)	160-65/0.3 (70)*	52.04 (51.89)	11.99 (12.24)	—
Et <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (1.54) + CH <sub>3</sub> CONCS (0.53)	1:1	Et <sub>2</sub> Sn(OPr <sup>i</sup> )(NCS) (white solid)	165-70/0.5 (20)*	40.26 (40.40)	4.81 (4.76)	285.0 (293.8)
Et <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (1.51) + CH <sub>3</sub> CONCS (1.03)	1:2	Et <sub>2</sub> Sn(NCS) <sub>2</sub> (yellow solid)	Decomp. at 130-35/0.3	40.06 (40.52)	9.32 (9.56)	—
Bu <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (2.64) + CH <sub>3</sub> COCN (0.52)	1:1	Bu <sub>2</sub> Sn(OPr <sup>i</sup> )(CN) (yellow solid)	165-70/0.4 (80)*	36.96 (37.35)	4.31 (4.40)	—
Bu <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (2.45) + CH <sub>3</sub> COCN (0.97)	1:2	Bu <sub>2</sub> Sn(CN) <sub>2</sub> (white solid)	195-200/0.5 (67)*	40.40 (41.67)	9.49 (9.83)	—
Bu <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (2.69) + CH <sub>3</sub> CONCS (0.77)	1:1	Bu <sub>2</sub> Sn(OPr <sup>i</sup> )(NCS) (yellow solid)	Decomp. at 170-80/0.5	33.73 (33.93)	3.87 (4.01)	340.0 (349.9)
Bu <sub>2</sub> Sn(OPr <sup>i</sup> ) <sub>2</sub> (3.02) + CH <sub>3</sub> CONCS (1.73)	1:2	Bu <sub>2</sub> Sn(NCS) <sub>2</sub> (white solid)	195-200/0.4 (40)†	34.81 (34.02)	7.87 (8.02)	351.0 (348.9)

\*Sublimed. †Distilled.

*Acetyl isothiocyanate* — Acetyl isothiocyanate was prepared by the reaction of potassium thiocyanate (vacuum dried) and acetyl chloride in benzene (~50 ml). The reaction mixture was refluxed for 6 hr under a fractionation column. Volatile fractions up to about 130° were slowly distilled out and rejected. The second fraction (130-33°) contained acetyl isothiocyanate as a yellow liquid having pungent smell. It was collected in 80% yield. The product was redistilled before use (Found: N, 13.80. Calc. for CH<sub>3</sub>CONCS: 13.86%).

*Reaction between triethyltin isopropoxide and acetyl cyanide* — A mixture of triethyltin isopropoxide (2.52 g, 0.009 mole) and acetyl cyanide (0.66 g, 0.009 mole) in cyclohexane (~40 ml) was refluxed for 2 hr. Removal of solvent under reduced pressure gave a white crystalline solid, which sublimed at 130-35°/0.5 mm (72% yield) (Found: Sn, 51.51; N, 5.82. Calc. for Et<sub>3</sub>SnCN: Sn, 51.22; N, 6.04%).

Other reactions of trialkyl- and dialkyltin isopropoxides with acetyl cyanide and thiocyanate have been carried out similarly and the results are summarized in Table 1.

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#### References

1. CAHOURS, A., *Ann. Chem.*, **122** (1962), 48.
2. SEYFERTH, D. & KAHLN, N., *J. org. Chem.*, **25** (1960), 809.
3. SEYFERTH, D. & KAHLN, N., *J. Am. chem. Soc.*, **82** (1960), 1080.
4. ANDERSON, H. H. & VASTA, J. A., *J. org. Chem.*, **19** (1954), 1300.
5. CUMMINS, R. A. & DUNN, P., *Aust. J. Chem.*, **17** (1964), 411.
6. LUIJTEN, J. G. A. & VAN DER KERK, G. J. M., *A survey and the chemistry and application of organotin compound* (Tin Res. Inst., Greenford, England), 1955.
7. VAN DER KERK, G. J. M. & LUIJTEN, J. G. A., *J. appl. Chem.*, **6** (1956), 49.
8. LORBERTH, J., *Chem. Ber.*, **98** (1965), 1201.
9. GORSI, B. L., KAPOOR, P. N. & MEHROTRA, R. C., *Indian J. Chem.*, **13** (1975), 1200.
10. GORSI, B. L., KAPOOR, P. N. & MEHROTRA, R. C., *Indian J. Chem.*, **14A** (1976), 406.

### Some Penta-coordinated Adducts of Cu(II)-β-Isopropyltropolonate with α- & γ-Picolines, Pyridine, Diethylamine & Imidazole

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The adduct formation of Cu(II)-β-isopropyltropolonate with some bases has been studied spectrophotometrically in benzene solution. All the bases form 1:1 adducts in which copper exhibits penta-coordination. The equilibrium constants have been obtained using a computer programme and the stability order for adduct formation is: γ-picoline > pyridine > diethylamine > imidazole > α-picoline.

WE have previously investigated the base adducts of Ni(II) and Co(II) β-isopropyltropolonates using an NMR technique<sup>1,2</sup>. Because of unfavourable relaxation time, the corresponding Cu(II) adducts could not be studied in a similar manner. Adduct formation with bases like pyridine, γ-picoline, α-picoline, imidazole and diethylamine was therefore studied by a spectrophotometric method and the results are described in the present note.

β-Isopropyltropolone (IPT) and imidazole (Koch-Light) were used as such. The other bases, α- and γ-picoline, pyridine (all BDH, LR) and diethylamine (Eastman) were stored overnight over sodium hydroxide pellets and distilled before use.

Cu(II)-β-isopropyltropolonate was prepared by slowly mixing 1 mole of copper acetate in 50% ethanol with slight excess of IPT (2 moles) in ethanol. The compound precipitated as green crystals after a few hours and was recrystallized from benzene-pet. ether.

The base adducts were obtained by slow recrystallization from the solution of the parent compound in the relevant base. However, only the γ-picoline adduct was found to be sufficiently stable in the solid state for use in physical measurements.

The electronic spectra in the range 400-800 nm were recorded on a Hitachi model 200-10 spectrophotometer while the infrared spectra of IPT, Cu(IPT)<sub>2</sub> and its γ-picoline adduct in KBr were obtained on a Perkin-Elmer spectrophotometer, model 21. The molecular weight determinations were made on a Hitachi apparatus.

Cu(IPT)<sub>2</sub> in benzene exhibits a broad absorption maximum at about 675 nm. Addition of bases brings about a bathochromic as well as a hyperchromic effect and the family of absorption spectra for increasing base concentration pass through an isobestic point at 598 nm.

Since  $\epsilon_a$ , the extinction coefficient of the adduct could not be obtained with certainty from experimental data,  $\epsilon_a$  along with the equilibrium constant for the adduct forming reaction was obtained by the method of Graddon<sup>3</sup>. The absorbance  $D$  at a particular wavelength for a given base concentration is given by

$$D = D_c + D_a$$

where  $D_c$  and  $D_a$  are the absorbances of the parent complex and the adduct respectively. Now if  $C$  is the total concentration of the parent complex and  $x$  be the amount of the adduct formed,

$$\epsilon \cdot C = \epsilon_0(C-x) + \epsilon_a x$$

where  $\epsilon_0$  and  $\epsilon_a$  are the extinction coefficients of the parent complex and the adduct respectively and  $\epsilon$  the observed value at a given base concentration, so that

$$x = \frac{C(\epsilon - \epsilon_0)}{\epsilon_a - \epsilon_0}$$

and the equilibrium constants  $\beta_1$  and  $\beta_2$  for the 1:1 and 1:2 adducts are given by

$$\beta_1 = \frac{x}{(C-x)(b-x)} \quad \text{and} \quad \beta_2 = \frac{x}{(C-x)(b-2x)^2}$$

where  $b$  is the concentration of the base added. Using a suitable computer programme, the trial