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Phenyl Isocyanate Interactions with Tin(IV) Halides

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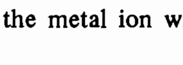
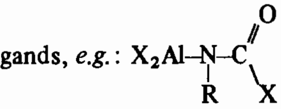
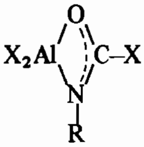
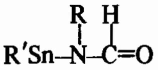
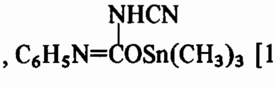
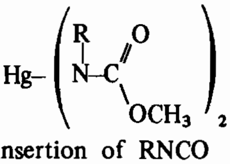
Studies of the interactions of phenyl isocyanate with SnX_4 (X = Cl, Br, I) in carbon tetrachloride solution, at ambient temperature, and of the solid products isolated are reported. $SnCl_4$ and $SnBr_4$ yielded 1:2 adducts with C_6H_5NCO, under these experimental conditions. These complexes were characterized as octahedral trans-$[SnX_4(OCNC_6H_5)_2]$; *the two phenyl isocyanate ligands are oxygen-bonded to the Sn^{4+} ion and occupy* trans *positions, relative to each other, in the first coordination sphere of this metal ion. Stabilization of the* cis-*isomers in the solid state is apparently sterically hindered, owing to the presence of the bulky phenyl substituent in the C_6H_5NCO ligand. The interaction of SnI_4 with phenyl isocyanate resulted in the formation of reaction rather than addition products. A solid precipitate, formed in low yield, appears to be a mixture of organic compounds and a tin complex. The N:O (2:1) and Sn:I (1:1) atomic ratios in this precipitate, in combination with the infrared evidence, suggest that the reaction proceeds via either insertion of C_6H_5NCO between Sn–I bonds or partial ionization of SnI_4 in the presence of the organic ligand, while the organic components of the solid product are mixtures or reaction products of C_6H_5NCO and phenylimido(C_6H_5N=) group derivatives.*

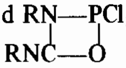
Introduction

A wide variety of reactions of organic isocyanates (RNCO; R = alkyl or aryl) with metal salts and complexes have been reported. Various adducts have been isolated, as follows: $AlX_3 \cdot RNCO$ (X = OC_2H_5, Cl, Br) [1–4], $[(C_2H_5)_2C_6H_5P]_2ReOCl_3 \cdot RNCO$, $[(C_6H_5)_3P]RhCl \cdot 2RNCO$ [5], $[(CO_3Fe(RNCO)_2Fe(CO)_3]$ [6], adducts with dibutyltin(IV) dilaureate [1], metal(II) naphthenates [7], $VOCl_3 \cdot 2RNCO$ [8], and $[(C_6H_5)_3P]_2Ni \cdot 2RNCO$ [9]. Several modes of coordination of RNCO in its adducts have been proposed, *viz.*: unidentate, O-bonded [1–4], bidentate bridging, C,N-bonded [6], bidentate, chelating, O,N-bonded [7], *etc.* The decomposition of $L_2ReOCl_3 \cdot RNCO$ (L = $(C_2H_5)_2C_6H_5P$) to the phenylimido(C_6H_5N=) ligand complex $L_2(C_6H_5N)ReCl_3$ and CO_2 was attributed to the formation of  as intermediate [5]. Phenylimido metal complexes are also formed by decomposition of $VOCl_3 \cdot 2C_6H_5NCO$, which yields $(C_6H_5N)VCl_3$ [8], and by reaction between C_6H_5NCO and $Ru_3(CO)_{12}$ (main product: $(C_6H_5N)Ru_3(CO)_{10}$) [10].

Quite frequently, the initial adduct formation is followed by insertion of RNCO between bonds of the metal ion with other ligands, *e.g.*:  $X_2Al{-}N(R){-}C(=O)X$ or  (X = Cl, Br) [4, 11],  $R'Sn{-}N(R){-}C(H){=}O$ [12],  $C_6H_5N{=}C(NHCN)OSn(CH_3)_3$ [13],  $Hg{-}(N(R){-}C(=O)OCH_3)_2$ [14], and several products of insertion of RNCO between metal–ethyl bonds (M = Al(III), In(III), Zn(II)) [4, 15–18]. Following the insertion of one RNCO molecule into a metal–ligand bond, additional RNCO groups can be inserted, one at a time, into the metal–RNCO bond. In this way, dimers, cyclic trimers (alkyl or aryl isocyanurates) (I) or linear polymers

(N-substituted 1-nylons) (II) of RNCO can be obtained under appropriate conditions. Thus, a dimer of C_6H_5-NCO was produced during its reaction with $AlCl_3$ [3], and trimers of type (I) were obtained by reaction of RNCO with organotin oxides and alkoxides or tin acetylacetonate [19] or metal cyanates [20]. On the other hand, RNCO is homopolymerized at low temperatures to amorphous [21] or crystalline [22] polymers of type (II), in the presence of a variety of inorganic or organometallic catalysts, including NaCN or sodium solutions in N,N-dimethylformamide, sodium benzophenone ketyl, sodium naphthalene [21], C_2H_5Li and $(C_2H_5)_2Be$ [22]. Nickel complexes, such as $Ni(bipy)_2$ (bipy = 2,2′-bipyridine) and $[(C_6H_5)_3P]_4Ni$, seem to catalyze the formation of mixtures of polymers of types (I) and (II) [9].

I II

A number of more complex interactions of RNCO with metallic compounds have been also reported, *i.e.*: reaction of bis(acetylacetonato)Cu(II) with C_6H_5NCO leads to the formation of the corresponding bis-chelate of Cu(II) with the 3-(N-phenylcarbamoyl)-2,4-pentanedionato ligand ($CH_3COC(NHC_6H_5)COCH_3$) [23]. Reaction of the polymeric $[NH_2Cr(OC_6H_5)_2]_x$ with C_6H_5NCO yields a mixture of $Cr(OC_6H_5)_2[N(CONHC_6H_5)CON(C_6H_5)CONHC_6H_5]$ and $Cr_{15}(OC_6H_5)_{20}(NH_2)_2(NH_3)(NHCONHC_6H_5)_6$ [24]. RNCO reacts with PCl_5 as follows: RNCO + PCl_5 → RN=CCl_2 + $POCl_3$ + RN=C=NR + $COCl_2$; intermediates proposed for this reaction include $RNPCl_3$ and  $\begin{matrix} RN-PCl_3 \\ RNC-O \end{matrix}$ [25]. Finally, an oxidative addition of p-ClC_6H_4NCO to $[(C_6H_5)_3P]_4Ni(0)$ leads to the formation of $[(C_6H_5)_3P]_2Ni^{II}Cl(p\text{-}C_6H_4NCO)$ [26].

These laboratories have previously reported on synthetic and characterization studies of tin(IV) halide adducts with O- [27] and O,N- [28] neutral ligands, as well as products formed by thermal decomposition of such adducts [29]. It was of interest to us to extend our studies on Sn(IV) complexes to the products of interaction between SnX_4 (X = Cl, Br, I) and C_6H_5NCO. The present paper deals with the syntheses and characterization of adducts of this ligand with $SnCl_4$ and $SnBr_4$ and with the reaction of phenyl isocyanate with SnI_4.

Experimental

Preparation of SnX_4 $2C_6H_5NCO$ Adducts (X = Cl, Br)

Fisher reagent grade CCl_4 was treated with molecular sieve 4A (Fisher, grade 516) for a period of 48 hr, to remove traces of water [30]. The dried CCl_4 was then used for the preparation of a 0.2 *M* solution of C_6H_5NCO (Eastman Kodak) and 0.1 *M* solutions of $SnCl_4$ and $SnBr_4$. Subsequently, 75 ml of the C_6H_5NCO solution were mixed at ambient temperature with 150 ml of the $SnCl_4$ or $SnBr_4$ solution. Precipitation was immediate in both cases (with yields exceeding 75% of the theoretical). The new solid complexes were separated by filtration, about 1 hr after their precipitation, washed with CCl_4 and stored in an evacuated desiccator over anhydrous $CaCl_2$. Analytical results (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) indicate that 1:2 adducts were formed in both cases, *i.e.*, found (calc.)%: $SnCl_4 \cdot 2C_6H_5NCO$ (light yellow powder): C 33.27 (33.71); H 2.23(2.02); N 5.65(5.62); Sn 23.42(23.80); Cl 28.91(28.43); $SnBr_4 \cdot 2C_6H_5NCO$ (tangerine orange crystals, yielding a lemon yellow powder upon grinding): C 24.68(24.85); H 1.78(1.49); N 4.31(4.14); Sn 17.84(17.54); Br 47.61 (47.24). Both of these adducts are stable in the atmosphere and soluble in polar organic solvents, including nitromethane. Attempts at melting point determinations revealed that no melting takes place at temperatures up to 200 °C; however, color changes were observed at elevated temperatures, as follows: $SnCl_4 \cdot 2C_6H_5NCO$: change of color to white at 160–190 °C, while the original precipitate collapsed to a very fine powder; $SnBr_4 \cdot 2C_6H_5NCO$: reduction of the size of the original crystals of this adduct at 160 °C, and change of the color to deep yellow at 172 °C. X-ray powder diffraction patterns suggest that the two new adducts are characterized by a rather low degree of crystallinity.

Reaction of C_6H_5NCO with SnI_4

Solutions of C_6H_5NCO and SnI_4 in CCl_4 were allowed to interact, under the conditions described above. This reaction resulted in the precipitation of a brownish-black solid in very small yields (less than 10%, on the basis of the amount of Sn present), analyzing as follows: C 66.33%; H 3.86%; N 11.22%; Sn 5.91%; I 6.52%; O (difference from 100%) 6.16%. This air-stable product is soluble in nitromethane and other polar organic solvents, and does not melt at temperatures up to 200 °C, but its color changes to deep yellow at 175 °C.

Infrared Spectral and Molar Conductivity Studies

Infrared spectra were obtained on KBr discs (4000–600 cm^{-1}) and on Nujol mulls between high-density polyethylene windows (700–100 cm^{-1}) by using Perkin Elmer 621 and 181 spectrophotometers, calibrated by reference to a polystyrene standard [28, 31]. Molar conductivities were determined on 10^{-3} *M* nitromethane solutions of the complexes at 25 °C, by using a Yellow Springs Instrument Co., Model 31, Conductivity Bridge and a cell

TABLE I. Pertinent Infrared Data for $C_6H_5NCO(L)$ and Its Adducts with SnX_4 (X = Cl, Br)[a], cm^{-1}.

L	$SnCl_4L_2$	$SnBr_4L_2$	Band Assignment
2282vs	2555ms,b	2560ms	ν_{NCO}(as)
b	1632m	1645m	$\nu_{C=O}$
b	1564vs	1560vs	$\nu_{C=N}$
1445m,sh	1480vvs	1479vvs	ν_{NCO}(sym)
632s,[c] 616m,sh,	638w,b, 624m, 609m,	640vw, 620m, 580m,	ν_{Ligand} (650–200 cm^{-1})
569s,[c] 496m,	570ms,sh, 559ms,	560m, 542m,b,	
459vw, 410vw,sh,	540ms,b, 529s,	529ms, 510m,	
384m, 246m	470vs, 381s,sh,	468vs, 384m,sh,	
	290s,sh, 240ms,vvb	288w,b	
	366vvs,vsp	362s,vsp	ν_{Sn-O}
	309vvs,b		ν_{Sn-Cl}
		225vvs,b	ν_{Sn-Br}

Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder; sp, sharp.

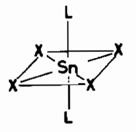
[a] Ir spectra obtained on a liquid film of the ligand and on KBr discs and Nujol mulls of the Sn(IV) complexes. The spectra of the SnX_4L_2 adducts are devoid of any absorptions attributable to the presence of water. [b] Ir spectrum of C_6H_5NCO at 1720–1445 cm^{-1}; 1720vw, 1665vw, 1599s, 1588m,sh, 1512s, 1480w,sh, 1451m, 1445m,sh. [c] The bands at 632 [41] and at 569 [40] cm^{-1} in the spectrum of C_6H_5NCO, have been considered by different research groups to involve contribution from the out-of-plane δ_{NCO} mode.

calibrated with a 10^{-3} *M* tetra-n-butylammonium perchlorate solution in nitromethane ($\Lambda_M = 92\ \Omega^{-1}\ cm^2\ mol^{-1}$ [32]).

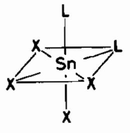
Results and Discussion

$SnCl_4$ and $SnBr_4$ Adducts with C_6H_5NCO

The isolation of 1:2 adducts between SnX_4 (X = Cl, Br) and phenyl isocyanate suggests that the synthetic conditions employed were mild enough as to favor the production of these adducts rather than compounds involving insertion of C_6H_5NCO between Sn^{4+} and X^- ions. The metal to ligand molar ratio in the new adducts is the most common for SnX_4 complexes with unidentate neutral ligands. Of interest, as far as the $SnX_4 \cdot 2C_6H_5NCO$ adducts are concerned, is the site of coordination of the ambidentate [33] phenyl isocyanate ligand, and the possible steric influence of the bulky phenyl substituent in this ligand on the assumption of the *trans*- (III) rather than the *cis*- (IV) arrangement of the two C_6H_5NCO groups. Regarding the latter consideration, the *cis*-geometry seems to be favored in solid SnX_4L_2 adducts, when the ligands do not introduce any significant steric hindrance [27, 34–38]. On the other hand, not only severely sterically hindered ligands, such as hexamethylphosphoramide (hmpa) [34, 35] and diisopropylmethylphosphonate(dimp) [27], but also ligands with relatively "mild" steric features (*e.g.*, tetrahydrofuran, tetrahydrothiophene, trimethylamine [36], pyrazine [39]) may force the assumption of the *trans*-isomeric configuration by the solid adduct [27, 34–39]. Equilibria between the *cis*- and *trans*-isomeric forms of SnX_4L_2 have been shown to exist in solutions of the adduct, containing excess ligand, even in the case of adducts with severely sterically hindered ligands, such as hmpa; the free energies of activation of the *cis*- and *trans*-forms of these adducts differ by only a few kcal/mol [35].



III



IV

Table I shows pertinent infrared data for C_6H_5NCO [40–43] and its new adducts with $SnCl_4$ and $SnBr_4$. The location of the $\nu_{C=O}$ and $\nu_{C=N}$ bands is not diagnostic of coordination of C_6H_5NCO through either O- or N-, since these modes occur at roughly the same frequency regions (1650–1640 and 1620–1524 cm^{-1}, respectively) in the spectra of compounds involving coordination of this ligand through either of these sites [4, 13]. However, the significant shifts of the two ν_{NCO} bands to higher wavenumbers indicate that coordination of the ligand is through the oxygen atom in the new tin(IV) halide adducts [4]. This is also supported by the identification of ν_{Sn-O} modes at 366–362 cm^{-1} in the spectra of both of these adducts. These bands, which are undoubtedly due to tin–ligand stretching vibrational modes, appear in the general region of occurrence of ν_{Sn-O} in tin tetrahalide adducts with neutral O-ligands (*e.g.*, triorganophosphine oxides 429–304 cm^{-1}, triorganoarsine oxides 425–373 cm^{-1} [38, 44], pyridine N-oxides 431–368 cm^{-1} [45], dimethylsulfoxide 482 cm^{-1} [38], C=O oxygen-bonded N,N-dialkylformamides 389–355 cm^{-1} [46]). In contrast, the ν_{Sn-N} mode in corresponding SnX_4L_2 adducts with unidentate N-ligands occurs at considerably lower wavenumbers (*i.e.*, alkyl cyanides 248–192 cm^{-1} [36, 47], pyrazine 212–202 cm^{-1} [39]). Hence, the assignment of the bands at 366–362 cm^{-1} in the spectra of the new adducts as ν_{Sn-O} is justifiable. The fact that C_6H_5NCO coordinates through oxygen in its adducts with Sn(IV) halides was not unexpected, since the corresponding adducts with AlX_3 (X = OC_2H_5, Cl, Br) and dibutyltin(IV) dilaureate also contain O-bonded C_6H_5NCO [1–4]. It should be noted, however, that no clear-cut predictions can be made regarding the affinity of Sn^{4+} for O- or N-ligands. In fact, not only products of insertion of either N- [12] or O- [13] bonded C_6H_5NCO between bonds of Sn^{4+} with other ligands have been reported, but it was also established that a similar neutral ligand, namely urea, is N-bonded in $SnCl_4(urea)_2$ and O-bonded in $SnBr_4(urea)_2$ [33, 48].

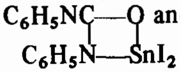
Regarding the arrangement of the two C_6H_5NCO ligands in the first coordination sphere of the Sn^{4+} ion in the new adducts, the ir evidence is definitely in favor of the *trans*-form (III) (D_{4h} symmetry). In fact, the very sharp character of the ν_{Sn-O} bands and the absence of any additional absorptions attributable to this mode, clearly show that the ir spectra of the new adducts involve single ν_{Sn-O} absorptions. Furthermore, single ν_{Sn-Cl} or ν_{Sn-Br} absorptions are also observed in the usual regions of occurrence of these vibrational modes [27, 34–36, 38, 39, 44–47, 49]. These features favor the *trans*- over the *cis*-configuration for the $SnX_4(OCNC_6H_5)_2$ adducts [27, 34–36, 38, 39, 49].

The molar conductivities of the new adducts (Λ_M, Ω^{-1} cm^2 mol^{-1} for 10^{-3} *M* nitromethane solutions at 25 °C: $SnCl_4(OCNC_6H_5)_2$ 6; $SnBr_4(OCNC_6H_5)_2$ 5) indicate that these compounds are nonelectrolytes [50]. Thus, on the basis of the overall evidence available, these complexes are formulated as *trans*-$[SnX_4(OCNC_6H_5)_2]$. It appears that the presence of the bulky phenyl substituent in C_6H_5NCO results in the introduction of sufficiently severe steric hindrance as to make the stabilization of the *cis*-isomers unfavorable.

Reaction of C_6H_5NCO with SnI_4

When SnI_4 was allowed to interact with C_6H_5NCO, under our experimental conditions, a quite different reaction occurred. In fact, neither the true adduct nor an insertion product was precipitated. The analytical results for the solid reaction product cannot be logically interpreted in terms of the presence of a single species. It is much more likely that we are dealing with a mixture, consisting mainly of an organic product, contaminated with smaller amounts of a Sn^{4+} complex involving one iodide ion per Sn atom. The ir spectrum of this solid product (4000–100 cm^{-1}) is a follows: 3200s, 3150m,sh, 3030 mw, 2920mw,sh, 2860w,sh, 2480w,b, 2350vw,sh, 2260vw,sh, 2110vvw, 1930vvw,b, 1865vvw, 1840vvw, 1788vvw, 1762vvw, 1705vvw,sh, 1692vw, 1670vw, 1613s,sh, 1580vvs, 1535vvs, 1500s,sh, 1444vs, 1429ms,sh, 1412mw,sh, 1392m, 1339s, 1298vs, 1280vvs, 1260m,sh, 1241m, 1216s, 1173s, 1141svs, 1109mw,sh, 1045w,vb, 960m, 917vw, 840vvw, 791w, 745vw,b, 700ms, 650mw, 631mw, 626mw,sh, 610vw, 555w,b, 504w, 482w,sh, 435vw,b, 407vw,sh, 375vw,b (extremely weak and broad bands with poorly defined maxima, characterize the spectrum at 350–100 cm^{-1}).

The preceding ir spectrum seems to rule out the presence of any of the known homopolymers of C_6H_5NCO (cyclic or linear) as major components of the isolated solid product. In fact, all these polymers exhibit medium to strong $\nu_{C=O}$ and other absorptions at 1870–1600 cm^{-1}, as follows (cm^{-1}): cyclic dimer 1709 [51]; phenyl isocyanurate(I) 1711–1695 [20, 51, 52]; crystalline linear homopolymer(II) several maxima at 1870–1620 [22]; amorphous linear homopolymer(II) 1709 [21]. In contrast, our product shows only very weak absorption at 1870–1620 cm^{-1}, with the first strong band with possible $\nu_{C=O}$ character occurring at 1613 cm^{-1}. Thus, it would appear that the product under discussion is probably formed by a complicated series of reactions. No serious attempts at the elucidation of these reactions can be made at this point; supplementary studies, aimed at the preparation of larger amounts of the solid product, as well as the isolation and identification of the various species remaining in solution, are to be undertaken in the near future. Nevertheless, the following remarks can be made: 1) Since the N to O atomic ratio in the solid product is about 2:1 and the Sn to I ratio is 1:1, half of the C_6H_5NCO oxygen and ¾ of the SnI_4 iodine seem to have been eliminated. 2) The ir spectrum of this product, at 1800–1500 cm^{-1}, shows similarities to those of various reaction products of C_6H_5NCO with Lewis acids or bases, *e.g.* (cm^{-1}): $R_2Al-OC(R')=NC_6H_5$ (R,R' = alkyl) 1605m, 1590–1585m, 1575–1545vs [16]; $Cl_3V=NC_6H_5$ 1600s, 1550w (differing from the spectrum of its precursor $VOCl_3(C_6H_5NCO)_2$: 1790–1780vw, 1700vs, 1670s, 1610s, 1600s, 1580s, 1510vs) [8]; $C_6H_5N=C(O)N(C_2H_5)_3$ 1715vw, 1690vw, 1640m, 1590ms, 1530ms,b [1]. 3) Both Sn^{4+} [53, 54] and I^- [55] reportedly catalyze reactions of RNCO with a variety of organic compounds.

On the basis of the preceding remarks, it seems reasonable to speculate that part of C_6H_5NCO reacts with SnI_4 to yield products involving either the phenylimido($C_6H_5N=$) group or some of its derivatives (*e.g.*, $C_6H_5N=C=NC_6H_5$ or $C_6H_5N=CI_2$), via intermediates such as  and $C_6H_5N=SnI_2$ [25]. The main component of the final product would then be produced by reaction of this initially formed species with unreacted C_6H_5NCO. As far as the tin-containing component of the final solid product is concerned, no conclusions regarding the nature of the ligands present can be reached, since medium to weak ir bands occur only in the ν_{Sn-C} region (630–490 cm^{-1}) [56], while ν_{Sn-O}, ν_{Sn-N} (490–190 cm^{-1}) and ν_{Sn-I} (below 200 cm^{-1}) regions are characterized by very weak absorptions.

The reactions between C_6H_5NCO and SnI_4, leading to the formation of the dark precipitate can be considered as proceeding via either insertion of C_6H_5NCO between Sn-I bonds or the formation of ionic species (*i.e.*, $[Sn(C_6H_5NCO)_nI_{6-n}]I_n$). Both these initial reactions would occur much more easily with SnI_4, relative to $SnCl_4$ or $SnBr_4$. In fact, the lattice energies in crystaline complexes of these salts decrease along the series Cl > Br > I, whilst the ease of ionization of SnX_4 decreases in the reverse order (*e.g.*, 2,2′-bipyridine N-oxide(L) forms, under the same synthetic conditions, the neutral $[SnX_4L]$ complexes for X = Cl, Br and the ionic species $[SnL_3]X_4$ for X = I [28]).

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