DONOR AND ACCEPTOR PROPERTIES OF SOME TRISUBSTITUTED OXY COMPOUNDS OF THE GROUP IV ELEMENTS[*]

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INTRODUCTION

In connection with our evaluation[1,2] of the validity of the "new" electronegativity scale[3,4] for the Group IV elements, it was of interest to examine in detail the chemistry of some of the compounds of these elements. Earlier, it was reported[3] that the trends in several sets of chemical reactions could be correlated with the "new" electronegativity scale. The reactions which were correlated, however, are so complex that the trends can be attributed to a number of factors. Although it has previously been concluded[2] that the set of numbers comprising this "new" scale cannot be interpreted as electronegativities, the possibility remains that these numbers constitute a set of reactivity parameters for compounds of the Group IV elements. It was decided that some relatively simple systems which could be investigated quantitatively should be examined to ascertain the validity of such a correlation. For this purpose the donor properties of the compounds $R_3MOC_6H_5$ (where R is CH_3 or C_2H_5 and M is C, Si, Sn and Pb) and the acceptor properties of $(C_6H_5)_3MOH$ were investigated. These properties do not correlate with the numbers comprising the "new" electronegativity scale. An explanation of the data is proposed and the essential factors determining this chemistry outlined.

A reversible dehydration reaction was observed when the bases, diethyl ether, N,N-dimethylformamide (DMF), and tetramethylene sulfoxide (TMSO), were added to carbon tetrachloride solutions of R_3SnOH and R_3PbOH:

$$2R_3MOH \rightleftarrows (R_3M)_2O + H_2O \qquad (1)$$

$$B + H_2O \rightleftarrows BH\text{—}O\text{—}H \quad \text{where B represents a base} \qquad (2)$$

This reaction obscures any hydrogen bonding interaction that might occur. It has also been found that the compounds, $(CH_3)_3SnOH$, $(C_2H_5)_3SnOH$, and $(C_2H_5)_3PbOH$ can be titrated with phenol in carbon tetrachloride solutions by using molecular sieves to absorb the water liberated by the reaction

$$R_3MOH + HOC_6H_5 \rightleftarrows R_3MOC_6H_5 + H_2O \qquad (3)$$

This affords a convenient method for the preparation of these compounds.

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EXPERIMENTAL

Miscellaneous silicon, german, tin, and lead compounds

The compounds listed below (together with appropriate references to the original literature) were prepared by conventional synthetic techniques. The elemental analyses of all the compounds prepared by these conventional techniques are not reported here, but were obtained and found, in each case, to be in excellent agreement with the "theoretical" values. Boiling points and melting points were also obtained and found to be in excellent agreement with the reported values.

1. Triphenylsilanol[5]
2. Triphenyllead hydroxide[5]
3. Triphenylgermanol[6]
4. Trimethyltin hydroxide[7]
5. Triphenyltin hydroxide[7]
6. Bis(tri-*n*-butyltin) oxide[7]
7. Bis(triethyltin) oxide[7]
8. Triethyltin phenoxide[8]
9. Trimethylsilyl phenoxide[9]

Triphenylcarbinol

Eastman White Label triphenylcarbinol was used without additional purification, m.p. 159–160°.

Bis(triphenyltin) oxide

Bis(triphenyltin) oxide was prepared by removing the water from a benzene suspension of triphenyltin hydroxide as the benzene azeotrope. The melting point of the product was 122–123°. (Found: C, 60.19; H, 4.31. $C_{26}H_{30}OSn_2$ calcd.: C, 60.39; H, 4.22 %.)

Triethyltin hydroxide

Triethyltin hydroxide was prepared by mixing equimolar quantities of bis(triethyltin) oxide and water. The solid was allowed to stand in a desiccator for one week over an aqueous 50 wt.-percent solution of sodium hydroxide; m.p. 49–50°, lit.[10] m.p. 43–47°. (Found: C, 32.59; H, 7.07. $C_5H_{16}OSn$ calcd.: C, 32.33; H, 7.24 %.)

Triethyllead hydroxide

Triethyllead hydroxide was prepared by the reaction between aqueous potassium hydroxide and triethyllead chloride (from tetraethyllead and anhydrous HCl[11]) in benzene solution[12]. The triethyllead hydroxide is quite heat-sensitive. Kept in a vacuum at 56°, it readily decomposes leaving a residue of diethyllead dihydroxide. (Found: C, 23.50; H, 5.13; Pb, 66.55. $C_6H_{16}OPb$ calcd.: C, 23.14; H, 5.18; Pb, 66.54 %.)

Triethyllead phenoxide

We were not able to prepare pure trialkyllead phenoxides by heating either tetraethyllead or tetramethyllead with phenol according to the procedure of Carothers[13]. The major product of these reactions is the dialkyllead diphenoxide which, in view of the heat sensitivity reported for trialkyllead compounds[14], could have arisen from a disproportionation of the trialkyllead compounds.

Titration of the trialkyl hydroxy compounds with phenol

A carbon tetrachloride solution approximately 0.2 M in triethyltin hydroxide was mixed with an equal amount of one 0.200 M in phenol. The cloudy solution which resulted was then stored over Linde 4-A molecular sieve for approximately one hour, during which time the solution became clear. The solution was then titrated to the end-point with an 0.05 M solution of either triethyltin hydroxyde or phenol. The end-point was taken as that point at which the hydroxyl stretching frequencies of $(C_2H_5)_3SnOH$, H_2O, and C_6H_5OH could not be detected in the region 3200–4000 cm^{-1} (solutions in 1.00-mm cells). The infra-red, ultra-violet, and nuclear magnetic resonance spectra of solutions prepared in this manner are identical to those obtained for solutions of triethyltin phenoxide in carbon tetrachloride.

Standard solutions of triethyl- or trimethyl-tin and -lead hydroxides could be determined with an accuracy of 4 % using this method, the equivalence point occurring at a mole ratio of 1:1 for hydroxide and phenol in accordance with equation (3).

Infrared spectra

Infrared spectra were recorded with a Beckman Model IR-7 spectrometer using matched solution cells with sodium chloride windows.

RESULTS

It has previously been shown that the change in the stretching frequency of phenol upon complexation to a donor, $\Delta\nu_{OH}$, is linearly related to the enthalpy of adduct formation[15]. This criterion was employed to obtain a measure of the donor strengths of some trialkyl phenoxy compounds of the Group IV elements. The results are contained in Table 1.

TABLE 1

PHENOL FREQUENCY SHIFTS ON HYDROGEN BONDING TO SOME GROUP IV TRIALKYL PHENOXY CMOPOUNDS

Compound	$\Delta\nu_H$	$-\Delta H$* (*kcal/mole*)
$(CH_3)_3SiOC_6H_5$	177	3.5
$(CH_3)_3SnOC_6H_5$	352	6.3
$(C_2H_5)_3SnOC_6H_5$	371	6.6
$(C_2H_5)_3PbOC_6H_5$	410	7.2

* Calculated from $\Delta\nu_{OH}$ by the procedure in reference 15.

The acidity of the compounds R_3MOH was examined by investigating the change in OH stretching frequency upon hydrogen bonding to the Lewis bases diethyl ether and tetramethylene sulfoxide. A relationship similar to that for phenol has not been established for these compounds. The assumption is made that the magnitude of the frequency shift is related to the acidity. The results are presented in Table 2.

West *et al.*[5] had previously reported a frequency shift of 26 cm^{-1} and one of less than 10 cm^{-1} for the hydrogen bonding interaction of diethyl ether with $(C_6H_5)_3PbOH$ and $(C_6H_5)_3SnOH$. The interpretation of the spectrum of $(C_6H_5)_3SnOH$ has been questioned*. In view of the higher electronegativity of lead than tin on the new scale this result was of importance to us. A stronger donor, TMSO, was employed in an attempt to accentuate any differences that may exist in the acidity of these compounds.

TABLE 2

HYDROGEN BONDING PROPERTIES OF TRIPHENYL HYDROXY COMPOUNDS

Compound[a]	ν_{OH}[b]	$\Delta\nu_{TMSO}$[c]	$\Delta\nu_{Et_2O}$[d]	$\Delta\nu_{Et_2O}$[e]
$(C_6H_5)_3COH$	3611	248	176	174
$(C_6H_5)_3SiOH$	3678	440	317	316
$(C_6H_5)_3GeOH$	3650	295	196	198

[a] Solutions 0.03 *M* in the hydroxy compounds and 0.25 *M* in TMSO or Et_2O. [b] Frequency of the free O–H band in cm^{-1}. [c] Frequency shift upon hydrogen bonding to TMSO, cm^{-1}. [d] Frequency shift upon hydrogen bonding to ethyl ether, cm^{-1}. [e] Frequency shift from reference 5.

Contrary to the previously reported results, it was found that $(C_2H_5)_2O$, TMSO and DMF caused both R_3SnOH and R_3PbOH to undergo a reversible dehydration reaction which obscures any hydrogen bonding interaction which may occur. The spectra of the system TMSO–$(C_2H_5)_3SnOH$ are contained in Fig. 1 and those of water–TMSO in Fig. 2.

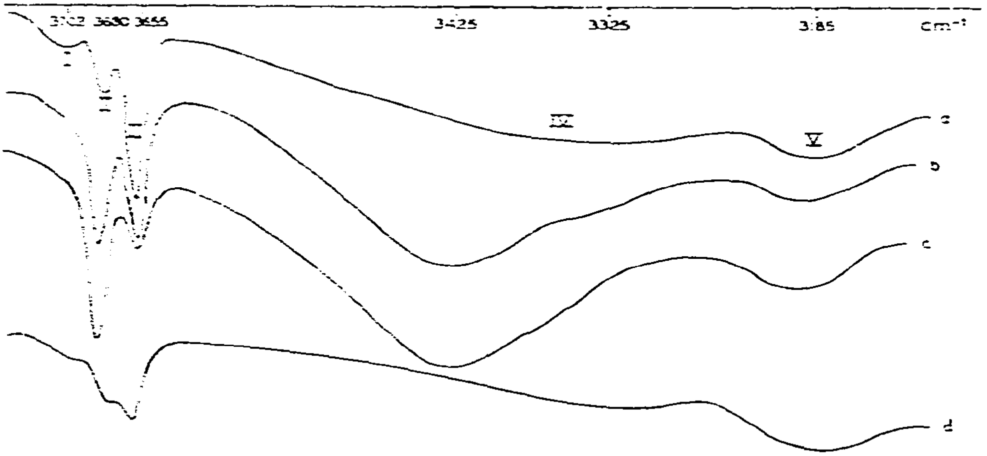

Fig. 1. Infrared spectra for the system TMSO–$(C_2H_5)_3SnOH$. (*a*), 0.08 *M* $(C_2H_5)_3SnOH$ in CCl_4; (*b*), 0.08 *M* $(C_2H_5)_3SnOH$ and 0.15 *M* TMSO in CCl_4; (*c*), 0.08 *M* $(C_2H_5)_3SnOH$ and 0.35 *M* TMSO in CCl_4; (*d*), 0.05 *M* $(C_2H_5)_3SnOH$ and 0.20 *M* $[(C_2H_5)_3Sn]_2O$ in CCl_4.

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* The assignment[5] of the band at 3645 cm^{-1} to O–H stretching vibration in $(C_6H_5)_3SnOH$ has been questioned by Kushlevsky, Simmons and Ross[14], who have reported that mulls of $[(C_6H_5)_3Sn]_2O$ also exhibit a band at 3645 cm^{-1}. However, neither concentrated carbon tetrachloride solutions of the alkyl oxides exhibited absorption bands in the region of the O–H stretching vibrations.

DISCUSSION

It is clear that neither the acceptor strengths of the compounds in Table 2 nor the donor strengths of the compounds in Table 1 can be correlated with the "new" electronegativity scale (C = 2.60, Si = 1.90, Ge = 2.00, Sn = 1.93 and Pb = 2.45).

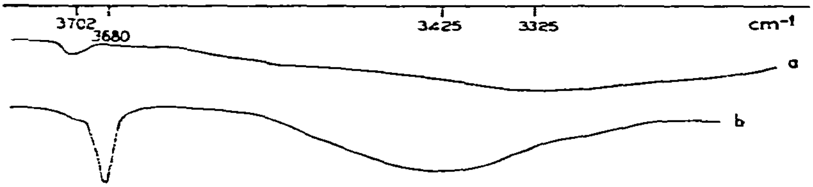

Fig. 2. Infrared spectra for the system TMSO–H_2O. (*a*), CCl_4 saturated with water; (*b*), 0.10 *M* TMSO in CCl_4 (initially saturated with water).

Lead is not behaving as though it were much more electronegative than tin in the $R_3MOC_6H_5$ compounds. Instead the lead compound is more basic than the tin. This correlates with a weaker lead–oxygen bond. The tin and lead hydroxy compounds, R_3MOH, are also very much alike in their behavior toward Lewis bases and phenol. Thus, in these compounds as in the addition compounds[17] of $(CH_3)_3SnCl$, $(CH_3)_3PbCl$ and $(C_2H_5)_3PbCl$, there is no indication that the chemical reactions can be correlated by assigning a higher electronegativity to lead than to tin.

The trends in the donor and acceptor strengths of the compounds of this family of elements are greatly influenced by π-bonding effects. We are in agreement with the proposal[5] that there is an appreciable amount of π-bonding between the lone pair oxygen filled orbitals and the empty *d*-orbitals of the central element in the silicon hydroxy compounds and that the π-bonding decreases in this series of compounds as the atomic number of the central element increases. The effect of π-bonding is to remove electron density from oxygen making the hydroxy compound more acidic and the phenoxy compound less basic. As the principal quantum number of the *d*-orbitals involved in π-bonding to oxygen increases, both decreased overlap and poorer energy matching of the orbitals contribute to less extensive π-bonding.

It is interesting that the hydroxy compounds of germanium are much poorer Lewis acids than those of the analogous silicon compounds. A considerable decrease in π-bonding is indicated in the germanium compound relative to silicon. If there is a minor reversal in the electronegativity of silicon and germanium this effect is masked by the far more important π-bonding effect. Since carbon is considerably more electronegative than germanium, the stronger acceptor properties of R_3GeOH than R_3COH indicate either some π-bonding in R_3GeOH or a steric effect in R_3COH which in valence bond terminology gives added importance to a structure of the type $R_3C^+OH^-$ in describing the ground state of this molecule. This steric effect would lengthen the C–O bond and decrease the acidity of this compound.

Dehydration reaction

In Fig. 1 are reproduced spectra of $(C_2H_5)_3SnOH$–TMSO systems which are representative of those recorded for the complete series of tin and lead compounds. A summary of the bands observed in the spectra of the carbon tetrachloride solutions (in the absence of TMSO) in the region 3100–3750 cm^{-1} is given in Table 3. Spectra for the system, TMSO–H_2O, are reproduced in Fig. 2.

TABLE 3

BANDS OBSERVED IN THE INFRA-RED SPECTRA OF TIN AND LEAD HYDROXY COMPOUNDS

Compound	I^a	II^a	III^a	IV^b	V^c
$(C_6H_5)_3SnOH$	3702	3680	3645	3325	3200
$(CH_3)_3SnOH$	3702	3680	3656	3325	3187
$(C_2H_5)_3SnOH$	3702	3680	3655	3325	3190
$(C_6H_5)_3PbOH$	3702	3680	3618	3325	3160
$4[(C_2H_5)_3Sn]_2O\cdot(C_2H_5)_3SnOH^{d,e}$	3702	3680	3655	3325	3180
$[(C_6H_5)_3Sn]_2O\cdot(C_6H_5)_3SnOH$	3702	3680	3656	3325	3200
Water	3702			3325	

[a] Values ± 1 cm^{-1}. [b] Values ± 10 cm^{-1}. [c] Values ± 5 cm^{-1}. [d] CCl_4 solution 0.20 *M* bis(triethyltin) oxide and 0.05 *M* triethyltin hydroxide. [e] Neither $[(C_2H_5)_3Sn]_2O$ nor $[(n\text{-}C_4H_9)_3Sn]_2O$ exhibit any absorption bands in the region of the O–H stretching vibrations.

Band I in the spectra can be assigned to "free" water vibrations[18]. Band II appears in all the spectra (including those for the TMSO–water systems) and can tentatively be assigned to the adduct, B^-–H–OH. Smith and Creitz[19] have shown that the absorption of the free O–H in singly-bridged alcohol dimers (RO–H–OR) occurs approximately 25 cm^{-1} lower than that of the free OH in monomers. Band III in the spectra can be assigned to an OH stretching vibration in the parent hydroxy compounds, R_3MOH[16]. Band IV can be assigned to the vibrations due to the species arising from the association of water with the strong Lewis bases, R_3SnOH, R_3PbOH, $(R_3Sn)_2O$ and $(R_3Pb)_2O$.

The assignment of the absorption bands and the conclusion that reactions (1) and (2) occur in carbon tetrachloride solutions of the tin and lead compounds seem reasonable since:

(*a*) Band III decreases markedly in intensity, whereas Band II increases markedly in intensity upon the addition of TMSO to the solutions;

(*b*) Band IV disappears upon the addition of TMSO to the solutions under consideration (and is replaced by the TMSO–water band) but the intensity of Band V is diminished only slightly;

(*c*) even the spectra of mixtures of $(C_2H_5)_3SnOH$ and $[(C_2H_5)_3Sn]_2O$ exhibit water bands; and

(*d*) in the spectra of mixtures of $[(C_2H_5)_3Sn]_2O$ and $(C_2H_5)_3SnOH$, Band IV is much weaker and Band V is stronger than in the spectra of $(C_2H_5)_3SnOH$ alone.

The infrared spectra of the systems, Et_2O–R_3MOH and DMF–R_3MOH, were similar to those for the TMSO–R_3MOH systems and were consistent with reactions (1) and (2). In no instance could an absorption band be distinguished unequivocally for an adduct, $[R_3MO\text{–}H\text{–}B]^-$. For the carbon, silicon, and germanium compounds, however, normal hydrogen-bonding interactions were observed.

In the reaction of tin and lead oxides with a number of acids (for example, thiophenol and acetylacetone), equilibrium is attained rapidly[20].

$$(R_3M)_2O + 2HA \rightleftarrows 2R_3MA + H_2O \qquad (4)$$

As in the reaction of phenol with the tin and lead hydroxides (see EXPERIMENTAL), the use of molecular sieves to force the reactions to completion may be of value in the synthesis, *in situ*, of tin and lead compounds, such as the phenoxides, which are sensitive to light and heat.

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SUMMARY

The donor and acceptor properties of the compounds $R_3MOC_6H_5$ (where R = CH_3 or C_2H_5 and M = C, Si, Ge, Sn and Pb) and $(C_6H_5)_3MOH$ were investigated in detail. The results cannot be correlated with the "new" electronegativity scale proposed for the Group IV elements. Changes in the extent of π-bonding between the central element and oxygen are proposed as the dominant effect giving rise to the observed trends. Contrary to previous reports no hydrogen bonding interaction could be detected between $(C_6H_5)_3SnOH$ or $(C_6H_5)_3PbOH$ and $(C_2H_5)_2O$. The donors $(C_2H_5)_2O$, $(CH_3)_2SO$ and $HC(O)N(CH_3)_2$ were all investigated in this study. In every instance a reversible dehydration reaction occurred. The infrared spectra of these systems is discussed. It was found that the compounds R_3MOH (where R is CH_3 or C_2H_5 and M is tin or lead) could be titrated with phenol in the presence of molecular sieves. This procedure may be of value in the synthesis of group IV compounds which are sensitive to light and heat.

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