tion of the origin of some absorptions. However, without infrared absorptions to even lower frequencies and Raman spectra, no conclusive assignments can be made.

Proton Magnetic Resonance Spectra.—The pmr spectra of the three phenoxides in acetonitrile solution are shown in Figure 4. The spectrum of $Na_2[(Mo_6Cl_8)(OC_6H_5)_6]$ (curve A) shows, between 2.71 and 3.58 ppm, the peaks of the phenyl protons, in addition to the signal of the solvent protons at 8.10 ppm. In the case of $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$ (curve B), in addition to the phenyl protons between 2.78 and 3.92 ppm, the signal of the methyl protons appears as a fairly sharp peak at 6.37 ppm. The peak at 8.13 ppm is due to the solvent. The ratio between the area of the methyl signal and that of the phenyl is appropriate for $Na_2[\{Mo_6(OCH_3)_8\}(OC_6H_5)_6]$. All these characteristics strongly support the cluster formulation used. In the spectrum of $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$ (curve C) the signal of the methyl protons collapses to a multiplet with two main peaks at 6.28 and 6.41 ppm. This splitting may be due to the fact that, upon introduction of some phenoxy groups in the cluster, the remaining methoxy groups become magnetically nonequivalent. An even more complicated situation exists in the case of the phenyl protons. In addition to ligand phenoxide ions, there are now magnetically nonequivalent cluster phenoxy groups. Indeed, the pattern of their pmr signal, between 2.42 and 4.13 ppm, is considerably more complex than in the other two derivatives. Again, the ratio between the total area of the phenyl signal and that of the methyl is exactly as required for $Na_2[\{Mo_6(OCH_3)_4(OC_6H_5)_4\}(OC_6H_5)_6]$.

Acknowledgment.—The partial support of this work by the Office of Naval Research is gratefully acknowledged. H. D. McLaughlin assisted in much of the experimental work, and our analytical department performed the elemental analyses. Thanks are especially due Dr. G. R. Leader for his assistance in the pmr portion of this work. The magnetic balance at Villanova University was kindly made available to us by Professor A. J. Leffler.

Notes

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The Tin-119m Mössbauer Isomer Shift and the Valence State of Tin in Transition Metal Compounds

BY D. E. FENTON AND J. J. ZUCKERMAN[1]

Received December 26, 1968

The reaction of tin(II) halides with transition metal halides has been extensively investigated,[2] and the products have been variously described as containing tin(II) donor groups or tin(IV)–metal bonds. The anionic products from platinum metal halides have been described as derivatives of tin(II) where the trihalostannate(II) ion acts as a donor ligand toward the platinum metal.[3] The infrared spectra of these compounds have been interpreted in terms of a σ-donating trichlorostannate(II) group,[3c,4] and the high *trans* effect,[3b] as well as infrared[5] and F^{19} nmr[6] data, has been used as evidence that the trichlorostannate(II) ion is a weak σ donor and a strong π acceptor. Two modes of reaction are suggested: reduction of the platinum metal halide by tin(II) followed by complexation with the remaining excess tin(II) species or ligand replacement of chloride by trichlorostannate(II). The replacement of the trichlorostannate(II) group as tin(II) from the anions by pyridine, *p*-toluidine, triphenylphosphine, and carbon monoxide[3a] is taken as evidence for the nature of tin in the anionic species.

Several reactions of tin(II) materials give products with tin formally in the IV oxidation state,[7] identical with those prepared from tin(IV) sources,[8] for example

$$\begin{tikzcd}
{[\pi\text{-}C_5H_5Fe(CO)_2]_2 + SnCl_2} \arrow[dr] & \\
& {[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2} \\
{[\pi\text{-}C_5H_5Fe(CO)_2]_2Sn(C_6H_5)_2 + HCl} \arrow[ur] &
\end{tikzcd}$$

π-$C_5H_5Fe(CO)_2I$ produces π-$C_5H_5Fe(CO)_2SnCl_2I$ in an analogous reaction which may proceed through an intermediate tin(II) chloride coordination with the metal followed by iodine migration.[9] The possibility of a tin(II) carbeneoid species whose insertion would result in a tin(IV) product has also been raised.[7,10]

We sought by the use of ^{119m}Sn Mössbauer spectroscopy to test the valence state of the tin atom in a typical series of tin–transition metal derivatives prepared from tin(II) chloride. It is the practice of inorganic chemists to distinguish the formal oxidation states of tin(II) and tin(IV) and further to write electronic con-

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figurations such as Sn[Kr]$4d^{10}5s^25p^0$ for tin(II) compounds, $5sp^3$ for covalent tin(IV) compounds, and $5s^0p^0$ for ionic tin(IV) species. The number of electrons in the 5s subshell decreases from 2 to 0 as the list is descended, and ^{119m}Sn Mössbauer isomer shift (IS) values seem to follow the same change.[11] Tetrahedral gray tin (α-tin) with an IS commonly quoted as *ca.* 2.10 mm/sec *vs.* an $^{119m}SnO_2$ source and its molecular tetrahedral tin cluster analog, tetrakis(triphenylstannyl)tin (IS = 1.33 ± 0.10 mm/sec),[12,13] can be regarded as derivatives of tin(IV). The usual form of tin metal (white tin, β-tin) reacts with hydrogen chloride to produce tin(II) compounds,[14] and its IS, commonly quoted as *ca.* 2.65 mm/sec,[15] may be taken as the dividing line between the two tin valencies: all tin(IV) compounds falling below and all tin(II) compounds above. That this is so was first noted in 1962[16] and the hypothesis has been used to show that the compounds of formula R_2Sn, believed to be organo derivatives of tin(II), are in fact tin(IV) species[17] as has been corroborated by chemical,[18] nmr,[19] and X-ray evidence.[20]

In this view the IS data displayed in Table I represent either the first reported violation of the hypothesis of the separation of tin(II) and tin(IV) IS values by β-tin,[21] or evidence that all of the tin–transition metal compounds listed should be considered as derivatives of tin(IV). Comparison may be made with the trichlorostannate(II) salt and with the organotin(IV) trihalides.

TABLE I

TIN-119m MÖSSBAUER PARAMETERS

	IS, mm/sec	QS, mm/sec
$KSnCl_3 \cdot H_2O^a$	3.51 ± 0.06	0.74 ± 0.12
$SnCl_3^{-\,a}$	3.54 ± 0.06	1.00 ± 0.12
$SnCl_2 \cdot 2H_2O^b$	3.63 ± 0.06	0.99 ± 0.12
$Sn[Co(CO)_4]_4{}^a$	1.96 ± 0.06	0
$Cl_3SnMn(CO)_5{}^c$	1.73 ± 0.05	1.56 ± 0.07
$Br_3SnMn(CO)_5{}^c$	1.84 ± 0.10	1.44 ± 0.10
$(C_6H_5)_3SnMn(CO)_5{}^c$	1.45 ± 0.07	0
$Cl_3SnFe[\pi\text{-}C_5H_5(CO)_2]^d$	1.74 ± 0.02	1.77 ± 0.02
$(C_6H_5)_3SnFe[\pi\text{-}C_5H_5(CO)_2]^d$	1.50 ± 0.02	0
$(Cl_3Sn)_5Pt[(C_2H_5)_4N]_3{}^a$	1.64 ± 0.06	1.53 ± 0.12
$(Cl_3Sn)_2Pt[(C_2H_5)_4N]_2Cl_2{}^a$	1.56 ± 0.06	1.61 ± 0.12
$(Cl_3Sn)_2Pt[(CH_3)_4N]_2Cl_2{}^a$	1.80 ± 0.06	1.61 ± 0.12
$(Cl_3Sn)_2Pt_3(C_8H_{12})_3CH_3NO_2{}^a$	1.50 ± 0.06	1.20 ± 0.12
$(Cl_3Sn)_4Rh_2[(CH_3)_4N]_4Cl_2{}^a$	1.90 ± 0.06	1.62 ± 0.12
$(Cl_3Sn)Rh[(P(C_6H_5)_3]_3{}^a$	1.78 ± 0.06	1.73 ± 0.12
$(Cl_3Sn)Ir[C_8H_{12}]_2{}^a$	1.80 ± 0.06	1.64 ± 0.12
$(Cl_3Sn)_2Ru[(CH_3)_4N]_2Cl_2{}^a$	1.93 ± 0.06	1.64 ± 0.12
$Cl_3Sn(n\text{-}C_4H_9)^{c,e}$	1.70 ± 0.10	3.40 ± 0.10
$Cl_3SnC_6H_5{}^f$	1.27 ± 0.09	1.80 ± 0.09

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The tin–metal and tin–halogen internuclear distances are also pertinent. On the basis of a careful examination of the available structural data, Rundle and Olsen assigned the covalent radii $r(Sn^{II})$ = 1.63 Å and $r(Sn^{IV})$ = 1.40 Å, giving the internuclear distances $d(Sn^{II}\text{–}Cl)$ = 2.62 Å and $d(Sn^{IV}\text{–}Cl)$ = 2.39 Å.[20] In $SnCl_2$, $SnCl_2 \cdot 2H_2O$, and $SnCl_3^-$ [IS = 3.51–3.63 ± 0.06 mm/sec], d(Sn–Cl) ranges from 2.54 to 2.78 Å,[20] while in $Cl_3SnIr(C_8H_{12})_2$ [IS = 1.80 ± 0.06 mm/sec] d(Sn–Cl) ranges from 2.384 to 2.406 Å.[22] We interpret these data as corroborating our assignment of tin(IV) in these compounds.

We have recently demonstrated that known nmr $J(^{119}Sn\text{–C–H})$, ^{119m}Sn Mössbauer IS and QS values, and structural data can be accommodated in the view that the nature of tin–transition metal compounds is controlled predominantly by the distribution of s electrons in the σ framework of the tin atom.[23] We submit that this can also be demonstrated for the known behavior of the compounds under examination here, if they are regarded as derivatives of tin(IV).

Experimental Section

Our $Ba^{119m}SnO_3$-equipped (New England Nuclear Corp.) cam-drive Mössbauer spectrometer and methods of data collection have been previously described.[24] All compounds were run at liquid nitrogen temperature. $KSnCl_3 \cdot H_2O$ was prepared by the method of Kamenar and Grdenic;[25] $Sn[Co(CO)_4]_4$ was kindly donated by Professor J. M. Burlitch of Cornell University; $(Cl_3Sn)_5Pt[(C_2H_5)_4N]_3$, $(Cl_3Sn)_2Pt[(C_2H_5)_3N]_2Cl_2$, and $(Cl_3Sn)_2Pt_3(C_8H_{12})_3CH_3NO_2$ were donated by Dr. G. W. Parshall of Du Pont; the other platinum metal complexes were prepared by the method of Young, *et al.*,[3a] to their standards of purity as determined by melting point and physical properties. The spectrum of the trichlorostannate(II) ion was run as a frozen ether extract

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(11) Interpretations of tin(II) data based only on covalent s–p hybridization correctly predict the order of IS values for all compounds but fluorides and oxides where s–p mixing may arise from electrostatic crystal field effects absent in the molecular compounds under examination here [J. D. Donaldson and B. J. Senior, *J. Chem. Soc., A*, 1796 (1966)], and recent Pople, Santry, and Segal SCMO calculations [N. N. Greenwood, P. G. Perkins, and D. H. Wall, Proceedings of the Symposium on the Mössbauer Effect, London, Dec 1967; Symposium of the Faraday Society, in press], the Fermi–Segre–Goudsmit semiempirical evaluation of $|\Psi_{5s}(0)|^2$ [V. I. Goldanskii, E. F. Makarov, and R. A. Stukan, *J. Chem. Phys.*, **47**, 4048 (1967)], Hartree–Fock nonrelativistic, self-consistent-field wave functions for various electronic configurations and charge states [S. L Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, *Phys. Rev.*, **159**, 239 (1967)], Liberman–Waber–Cromer relativistic wave functions [J. K. Lees and P. A. Flinn, *J. Chem. Phys.*, **48**, 882 (1968)], and an LCAO–MO treatment approximating LCAO–MO–SCF wave functions for tin [M. L. Unland and J. H. Letcher, *ibid.*, **49**, 2706 (1968)] all agree on the excellent correlation between s-electron density and IS values for tin(IV) compounds.

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from a solution of tin(II) chloride containing hydrochloric acid.[26,27]

Acknowledgment.—We wish to thank Mr. N. W. G. Debye for assistance with obtaining the Mössbauer data and for the preparation of the trichlorostannate(II) ion and Professor J. M. Burlitch of the Department of Chemistry, Cornell University, and Dr. G. W. Parshall of the Central Research Department of E. I. du Pont de Nemours and Co. for the donation of some compounds. Our work is supported by the National Science Foundation under Grant GP-9249.

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Evidence for a Trigonal-Prismatic Activated Complex in the Solid-State Racemization of Tris(1,10-phenanthroline)nickel(II) Perchlorate Dihydrate

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Received December 2, 1968

In 1964 Schmulbach, *et al.*,[1] investigated the effect of pressure on the solid-state racemization of $[Fe(phen)_3](ClO_4)_2$ and $[Ni(phen)_3](ClO_4)_2$. A negative volume of activation was observed which was interpreted as being consistent with a Bailar twist[2] type of mechanism. The effect of water on the racemization process was not investigated, however, and activated complexes containing water could not be ruled out. Recently, evidence has been presented in support of a Bailar twist mechanism for the solid-state racemization of $K_3[Co(C_2O_4)_3]\cdot xH_2O$ at very high pressures.[3] An unusually small activation energy and frequency factor were found for this process. This communication reports the results of a further investigation of the activation parameters for the high-pressure solid-state racemization of tris(1,10-phenanthroline)nickel(II) perchlorate. It was hoped that a comparison of the results of such an investigation with the results previously reported for the $K_3[Co(C_2O_4)_3]$ system would shed some light on the general nature of the Bailar twist mechanism.

Experimental Section

Apparatus.—The high-pressure apparatus used here was similar to that described previously.[4] Pressures were maintained constant to within 1 or 2% using an air-driven hydraulic pump purchased from the High Pressure Equipment Co., Erie, Pa., and were measured with a Heise gauge accurate to *ca.* 0.5%. Samples were prepared as described in ref 3 and subjected to pressures ranging from 10,000 to 40,000 atm. Except for the determination of the volume of activation, temperatures were controlled to within ±0.5° with a thermistor–Wheatstone bridge assembly and were monitored with a Sargent SR recorder. Samples used for the determination of ΔV^* were run at room temperature which was 21 ± 2°. After their removal from the high-pressure apparatus, all of the samples were analyzed polarimetrically in 50 vol % acetone–water at 589 mμ on a Rudolph Model 80 polarimeter with Model 200 photoelectric attachments.

***d*-$[Ni(phen)_3](ClO_4)_2\cdot 2H_2O$.**—This complex was prepared and resolved according to the procedure of Kauffman and Takahashi[5] and kept in a desiccator over silica gel.

For the investigation of the effect of water on the racemization rate a portion of optically active material was divided into two parts. One part was stored over P_2O_5 while the other was placed in a desiccator over a saturated solution of KNO_2 (45% relative humidity). Analyses for Ni were done polarographically after wet-washing of the complex with H_2SO_4–HNO_3 and the water content of the samples was obtained as the difference between the actual sample weight and the weight of "anhydrous" $[Ni(phen)_3](ClO_4)_2$ calculated from the Ni analyses.

Results

The volume of activation, ΔV^*, is given by the equation[4]

$$\left[\frac{\partial \ln \ln ([\alpha_0]/[\alpha_t])^{1/2}}{\partial p}\right]_{t,T} = -\frac{\Delta V^*}{RT}$$

where $[\alpha_t]$ is the specific rotation of the sample subjected to a pressure p for a time period t and $[\alpha_0]$ is the specific rotation of a control sample which had not been subjected to pressure. No changes were observed in the specific rotation of the control samples over a period of several months. A plot of $\ln \ln ([\alpha_0]/[\alpha_t])^{1/2}$ *vs.* p should yield a straight line of slope $-\Delta V^*/RT$. The linear least-squares slope obtained from the data in Table I gives a value of -1.00 ± 0.13 cm^3 mol^{-1} for ΔV^*, in good agreement with the values -1.10 ± 0.14 and -1.08 ± 0.22 cm^3 mol^{-1} obtained by Schmulbach, *et al.*[1]

The activation energy for this reaction may be obtained from the equation[3]

$$\left[\frac{\partial \ln \ln ([\alpha_0]/[\alpha_t])^{1/2}}{\partial (1/T)}\right]_{p,t} = \frac{-E_a}{R}$$

A plot of $\ln \ln ([\alpha_0]/[\alpha_t])^{1/2}$ *vs.* $1/T$ should give a straight line of slope $-E_a/R$. A linear least-squares treatment of the data in Table II yields an activation energy of 2.40 ± 0.31 kcal mol^{-1}. The frequency factor, calculated from the least-squares intercept, has a value of *ca.* 3×10^{-5} sec^{-1}.

In an attempt to exclude, as possible mechanistic paths, transition states which contain water in the coordination sphere, the effect of water on the reaction rate was examined. Samples containing different amounts of water were subjected to the same conditions of pressure, temperature, and time under pressure. The results of these experiments are presented in Table III. It will be noted that in each case the sample con-

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