

Figure 2.—Ionization efficiency curves representative of data from which the values plotted in Figure 1 were taken at the 1% level; the curves, left to right, are for compounds Ic, IIc, IIIc, and IVc.

energy spread.¹⁵⁻¹⁷ There is evidence that for some mechanisms of intersystem crossing (but not all) energy transmission to the metal in the rhodium complex Ic is an inefficient process as the weak influence of spin-orbit coupling on triplet-state lifetimes indicates.¹³ Otherwise there is little precedent for this model, since ionization usually occurs from the orbital of highest energy in the entire molecule.¹⁸

Alternatively, the possibility exists that substitution in one ring influences the ionization potential of the whole system so greatly that it is improper to speak of localization on an individual ring. Again in organic systems, π systems of the same molecule, perpendicular to each other but in close proximity, influence each other's energy manifolds dramatically.¹⁹

Finally, the magnitude of the shift of the IP (1.05 ± 0.05 eV for three groups) on nitration of the Rh(III) complex differs from the magnitude of the same shift for the Cr(III) complex (0.75 ± 0.08 eV). This difference is real, as a review of our error analysis shows. Interior points fall close to the line in these examples; the usual deviation from anticipated linear correlations²⁰ produced by our method is on the order of 0.02–0.03 eV. Consequently, there is a distinct difference between the susceptibility of the ionization potential to the substituent in the Cr(III) series and in the Rh(III) series. This fact is difficult to reconcile with the picture in which ionization occurs entirely from the ligand in both systems and indicates that some other picture—possibly one of those we have noted above for both systems or different models for each system—must be maintained.

(15) Even at 4.5 orders of magnitude below the normal intensity of the molecular ion we do not detect breaks in the curve which might be expected if inefficient (1%) ionization processes existed from other orbitals besides the one which produces ions efficiently, a model suggested by photoelectron spectroscopy studies.¹⁶ We note that present-day photoelectron spectroscopy does not include mass analysis.¹⁷

(16) D. R. Lloyd, *Chem. Commun.*, 868 (1970).

(17) Note the likely error in ref 16: S. Evans, A. Hamnett, and A. F. Orchard, *ibid.*, 1282 (1970).

(18) For a demonstration of this in organic molecules, see H. J. Svec and G. A. Junk, *J. Amer. Chem. Soc.*, **89**, 790 (1967).

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(20) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *J. Amer. Chem. Soc.*, **92**, 519 (1970).

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(22) F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

(23) C. G. Pitt, M. S. Habercom, M. M. Bursey, and P. F. Rogerson, *J. Organometal. Chem.*, **15**, 359 (1968).

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Mössbauer Spectroscopy of Tin(IV) Oxyhalides

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Of the numerous parameters which can be extracted from ¹¹⁹Sn Mössbauer spectra, the isomer shift (IS) and quadrupole splitting (QS) have been of greatest interest to the chemist.² In relating the IS of tetrahedral tin-halogen compounds, SnX₄, to other parameters which describe the bonding interaction between the metal atom and its ligands, it was noted³ that for X = Cl, Br, or I, there is a linear relationship between the ligand electronegativity and the IS extracted from the Mössbauer spectrum. Such an IS–electronegativity correlation has recently been extended to octahedral SnX₆²⁻ complexes,^{4,5} making use of Mulliken electronegativities. For both the tetrahedral and octahedral compounds it is observed that the isomer shift decreases as the electronegativity increases (Figure 1). From the relationship between the IS parameter and the electronic wave functions for the s electrons surrounding the ¹¹⁹Sn nucleus it is by now well established⁶ that a decrease in the isomer shift implies a decrease in the 5s electron density at the nucleus assuming that all measurements either are made using the same ¹¹⁹Sn source or (preferably) are referred to a standard absorber.⁷

A similar linear correlation for trimethyltin halides is also observed, despite the fact that there are significant structural differences between (CH₃)₃SnF (which is a nearly trigonal-bipyramidal polymer⁸) and (CH₃)₃SnI (which can be described as having a distorted tetrahedral structure). It should be noted, however, that the slope d(IS)/dχ for these compounds is very much

(1) Fullbright–Hayes Scholar, 1968–1969.

(2) For a general review of this field, see V. I. Gol'danskii and R. H. Herber, Ed., "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

(3) V. I. Gol'danskii, *At. Energy Rev.*, **4**, 3 (1963); see also the discussion by M. Cordey-Hayes and by V. I. Gol'danskii and E. F. Makarov in ref 2.

(4) R. H. Herber and H.-S. Cheng, *Inorg. Chem.*, **8**, 2145 (1969).

(5) C. A. Clausen, III, and M. L. Good, *ibid.*, **9**, 817 (1970).

(6) G. T. Emery and M. L. Perlman, *Phys. Rev. B*, **1**, 3885 (1970).

(7) All IS values quoted in the present discussion are with respect to the center of a room-temperature BaSnO₃ (or SnO₂) Mössbauer spectrum.

(8) H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc., London*, **85** (1963); *J. Chem. Soc.*, 2332 (1964).

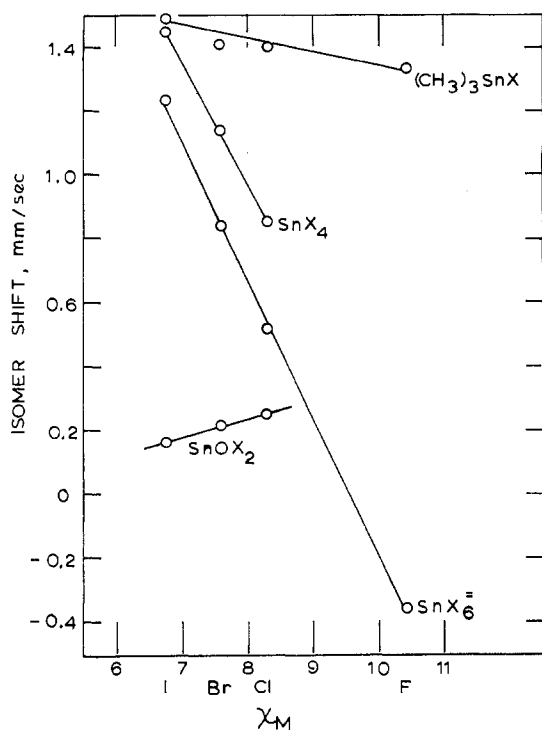


Figure 1.—Isomer shift–ligand electronegativity (χ_M) correlation for the compounds discussed in the text. The isomer shift is with respect to the centroid of a room-temperature BaSnO_3 spectrum. The slopes of the four lines shown: SnOX_2 , +0.0592; SnX_6^{2-} , -0.430; SnX_4 , -0.391; $(\text{CH}_3)_3\text{SnX}$, -0.039.

smaller than it is for the tetrahedral or octahedral halogen compounds. This fact can be accounted for by invoking Bent's rule⁹ from which it is inferred that the Sn–X bonds involve increased p character and the CH_3 –Sn bonds increased s character, relative to the sp^3 or sp^3d basis set. As the electronegativity of the halogen is increased, electron density is transferred from the metal to the halogen and the resultant buildup of charge on the metal atom is partially reduced by electron transfer from the methyl group to the Sn. Since the former involves an excess of p character and the latter an excess of s character, the relative change in the IS is reduced both by the decrease in shielding of the 5s electrons by the reduced 5p density and by a relative increase in the 5s electron density by the transfer of charge from CH_3 to Sn. These two effects combine to give a very much smaller change in the IS parameter per unit change in the electrogenativity of the ligand.

In an extension of these systematics we have examined the Mössbauer parameters of three tin(IV) oxyhalides, and the pertinent results are summarized in Table I. (The fourth compound in this series, Sn-

TABLE I
MÖSSBAUER PARAMETERS FOR TIN(IV) OXYHALIDES (80°K)

Compd	IS, ^{a,b} mm/sec	QS, ^b mm/sec	Γ , ^{b,c} mm/sec
SnOCl_2	0.25	0.72	1.12
SnOBr_2	0.22	0.79	1.12
SnOI_2	0.16	0.88	1.08

^a With respect to BaSnO_3 at 294°K. ^b All values ± 0.05 mm/sec. ^c Full width at half-maximum, uncorrected.

(9) H. A. Bent, *J. Inorg. Nucl. Chem.*, **19**, 43 (1961); *Chem. Rev.*, **61**, 275 (1961).

OF_2 , has a different structure—presumably octahedral¹⁰—and has not been included in the present measurements.) It is immediately apparent from these data (as shown graphically in Figure 1) that for these compounds the IS parameter *increases* as the ligand electronegativity increases, in contrast to the observations reviewed above. This fact can be understood in terms of the changes in the O–Sn and Sn–X bond character which occur as X changes from Cl to Br to I, as well as being due to the consequences of the changes in steric requirements of the two halogen atoms. From the near constancy of the Mössbauer parameters (Table I), as well as the infrared data of Dehnicke,¹⁰ it may be inferred that the three oxyhalides are essentially isostructural. Despite the observation of a molecular weight which corresponds to a trimeric unit in POCl_3 , on the basis of which Dehnicke has proposed a cyclic structure for SnOCl_2 , the presence of a single infrared-active mode in the Sn–O region argues against the presence of such a structure in the solid. While the low solubility of these compounds in nonpolar solvents suggests a polymeric (chainlike) configuration, the presence of both a symmetric and asymmetric Sn–X band in the ir spectra must be considered as indicative of a nonlinear configuration of the X–Sn–X moiety.

In this context it is assumed that the metal atom hybridization can be described as corresponding to sp^2 , with a lone pair occupying the third (nonbonding) p orbital. In this view, as the halogen ligand becomes more electronegative (*i.e.*, $\text{I} \rightarrow \text{Br} \rightarrow \text{Cl}$), charge is transferred from the metal to the halogen *via* a bond which increases in p character. To offset this charge transfer, electron density flows from the oxygen atom to the metal *via* an interaction which increases in s character. Both the decrease in 5p electron shielding *via* the first of these processes and the increase in the 5s electron population *via* the second serve to increase the 5s electron density at the tin nucleus, and hence the isomer shift increases as the halogen becomes more electronegative, in consonance with observation.

There is also an accompanying effect due to the change in the size of the halogen ligands. As X becomes larger, the X–Sn–X bond angle increases and hence the orbital overlap of halogen p orbitals and metal sp^2 orbitals becomes less favorable and the metal orbitals tend toward an sp-type hybridization. Since there is less charge transfer *from* the metal to the halogen as the electronegativity of the latter decreases, this change in the hybridization may account in part for the observed variation in the IS parameter.

Finally, it should be noted that the QS parameters in the tin oxyhalides, while significantly larger than those observed for other tin(IV)–mixed-halogen complexes,^{4,5} are considerably smaller than those reported for trigonal-bipyramidal Sn(IV) molecules such as $(\text{CH}_3)_3\text{SnF}_2$ or $(\text{CH}_3)_3\text{SnCN}$.¹¹ It has been generally recognized that the major contribution to the electric field gradient tensor which governs the magnitude of QS in ¹¹⁹Sn Mössbauer spectra arises from an imbalance in the 5p-orbital population around the metal atom. On the basis of the assumed model, it is seen that the nonbond-

(10) K. Dehnicke, *Z. Anorg. Allg. Chem.*, **308**, 72 (1961); **335**, 279 (1965); *Chem. Ber.*, **98**, 280, 290 (1965).

(11) B. Gassenheimer and R. H. Herber, *Inorg. Chem.*, **8**, 1120 (1969); R. H. Herber, S. C. Chandra, and Y. Hazony, *J. Chem. Phys.*, **53**, 3330 (1970).

ing (lone pair) electrons in the p orbital which is orthogonal to the plane of the ligands make a contribution to the field gradient tensor which almost compensates for the contributions of the p electrons involved in the metal-ligand interactions. The resulting charge distribution has nearly (but not identically) cubic symmetry around the metal atom as inferred from the magnitude of the QS parameter which is observed. The small (but significant) increase in QS as the halogen electronegativity decreases and size increases may be related to the change in hybridization referred to above and reflects the departure from orthogonality of the p-electron population. A more detailed interpretation of the presently available data does not seem warranted at the present time.

Experimental Section

The three tin oxyhalides were prepared by literature methods¹⁰ by the ozonization of the anhydrous tetrahalides and mounted as solid samples (~10 mg of Sn/cm²) in standard sample holders. The constant-acceleration Mössbauer spectrometer has been described earlier¹² and was calibrated using NBS 0.8-mil 99.9% natural iron foil. The sample temperatures were 80 ± 1°K by calibrated thermocouple. All ¹¹⁹Sn spectra were run using a room-temperature BaSnO₃ source, and zero relative velocity was determined experimentally from a room-temperature BaSnO₃-BaSnO₃ spectrum. Spectra were computed by using a standard curve-fitting program¹¹ in which the two line widths (but not intensities) were assumed to be identical. The straight lines shown in Figure 1 represent least-squares fits to the data.

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(12) See Chapter by N. Benczer-Koller and R. H. Herber in ref 2.

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Substitution Reactions of Oxalato Complex Ions. IX. The Kinetics of the Anation Reaction of Aquo-hydroxobis(ethylenediamine)cobalt(III) Ion by Oxalate in Basic Aqueous Solution

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The preceding paper in this series² reported the results of a study of the reactions in strongly acidic solutions (pH < 1) of the system analogous to that of the present study, where, however the reactants were limited essentially to *cis*-Co(en)₂(H₂O)₂³⁺ (en = ethylenediamine) and the two oxalate species H₂C₂O₄ and HC₂O₄⁻. As one shifts to higher pH, the system exhibits much greater complexity due to the various acid-base and *cis*-*trans* equilibria of the diaquo complex, as first elucidated by Bjerrum and Rasmussen³ and re-

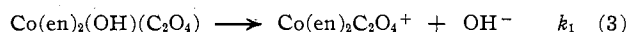
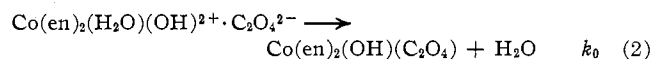
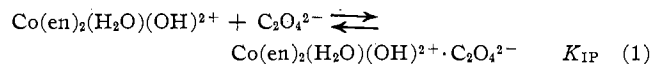
(1) University Research Fellow, State University of New York at Buffalo, 1968; on leave from the Department of Chemistry, University of Hong Kong.

(2) Part VIII: P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).

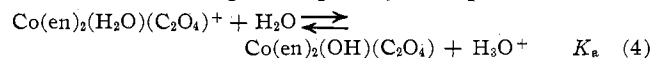
(3) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

cently further clarified by Lincoln and Stranks⁴ in a phosphate anation study. Above pH 7, the only oxalate species present in measurable amount is C₂O₄²⁻, while the reactant complex is made up of a mixture of the *cis* and *trans* forms of the ions Co(en)₂(H₂O)(OH)²⁺ and Co(en)₂(OH)₂⁺ as defined by the appropriate equilibrium constants.^{3,4}

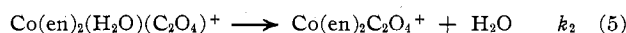
It was previously predicted² that the mechanism of oxalate anation in solutions of low acidity should be according to the reactions



Further, it was predicted that the hydroxooxalato intermediate formed in reaction 2 would prove to be identifiable, in contrast to the related aquooxalato species which was assumed to appear as an intermediate in the acidic system. The latter species is related to the uncharged complex by the equilibrium



The predictions were based on the known very much higher lability of the hydroxo-aquo complex as compared to the diaquo⁵ and the greater difficulty of dislodging hydroxide as compared to water ligand, suggesting that reaction 3 would take place less rapidly than its analog in acidic solution



In the present work, the anation has been studied in the range 7.3 < pH < 9.9 and the uncharged complex compound Co(en)₂(OH)(C₂O₄) has been identified in agreement with expectation. In addition, rate constants of some of the possible reactions have been determined and some suggestions made concerning the stereochemistry of these processes. The results, together with those obtained in an earlier study⁶ of the reverse of reaction 3, enable a reasonably complete mechanistic assessment of this anation-hydrolysis system over a wide range of pH.

Experimental Section

Aquo-hydroxobis(ethylenediamine)cobalt(III) nitrate was prepared by standard procedure.⁷ To observe the rate of appearance of the nonionic unidentate oxalato intermediate, a weighed quantity of the aquo-hydroxo salt was dissolved in a known volume of water previously brought to reaction temperature.^{8,9} This solution was mixed with a known volume of sodium oxalate solution of the desired concentration, appropriately buffered at the same temperature, and with its ionic strength adjusted with sodium nitrate. Samples were withdrawn at regular time intervals and passed through a column of mixed ion-exchange resin.¹⁰ The effluent and pure-water washings, containing only the uncharged Co(en)₂(OH)(C₂O₄) complex, were acidified, made up to a known volume, and allowed to stand overnight before analysis

(4) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 1745 (1968).

(5) W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961).

(6) S. Sheel, D. T. Meloon, and G. M. Harris, *Inorg. Chem.*, **1**, 170 (1962).

(7) The material used was obtained in this laboratory by Dr. P. M. Brown by crystallization from an aqueous solution of *cis*-Co(en)₂(H₂O)(OH)(NO₃)₂. The latter was prepared by neutralizing *cis*-Co(en)₂(H₂O)₂(NO₃)₃ with 1 equiv of NaOH (see ref 2 for preparation methods of the diaquo species).

(8) The aquo-hydroxo complex is of course in *cis*-*trans* equilibrium in an approximately 60:40 ratio. This equilibration is very rapid.⁹

(9) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

(10) The mixed-bed column consisted of Dowex 50W-X8 resin in the Na⁺ form and Dowex 1-X8 in the NO₃⁻ form, 20-50 mesh.