# Correspondence

## Halogen Electronegativity and Isomer Shifts of Tin Compounds. Another Example of the Importance of Charge Capacity

*Sir:*

There has been considerable recent interest in $^{119}$Sn Mössbauer spectroscopy as a probe of the electronic environment of the tin nucleus and, hence, of the bonding in tin compounds. One of the earliest correlations found is that between the isomer shift (IS) and the electronegativity ($\chi$) of the substituents.[1-5] This effect was first shown for the tetrahedral halides[1-3] and then extended to the octahedral hexahalostannate(IV) complexes.[4,5] For both series of compounds plots of isomer shift *vs.* the sum of the substituent electronegativities are linear. The hexahalostannates provide the better test of the phenomenon since, in addition to the four species $SnX_6^{2-}$, there are several mixed species of the general type $SnX_4Y_2^{2-}$. Herber and Cheng[4] found a good correlation between the isomer shift in these anions and the summation of the Pauling electronegativities[6] except for three species: $SnBr_4I_2$,$^{2-}$ $SnCl_4I_2^{2-}$, and $SnF_6^{2-}$. They attributed the deviation of the former two species to possible distortions of these anions resulting from the cis[7] iodo ligands. Clausen and Good[5] reinvestigated the series and obtained larger isomer shifts for the iodo anions such that they were no longer at variance with the remaining complexes. They also claimed that the apparent discrepancy for $SnF_6^{2-}$ disappeared if Mulliken electronegativities[8] were used instead of Pauling values. Cheng and Herber[9] concurred with this interpretation and extended the treatment to the electronegativity of nitrogen.

TABLE I

COMPARATIVE VALUES OF GROUND-STATE[a] AND VALENCE-STATE[b] IONIZATION ENERGIES AND RESULTING ELECTRONEGATIVITIES

| | Values of Clausen and Good[c] | | | | Values of Jaffé, *et al.*[d] | | | |
|---|---|---|---|---|---|---|---|---|
| Element | Ionization energy, eV | Electron affinity, eV | Mulliken electroneg, eV | Pauling electroneg[e] | Ionization energy, eV | Electron affinity, eV | Electron electroneg, eV | Mulliken electroneg[e] |
| F | 17.418 | 3.448 | 10.43 | 3.30 | 17.418 | 3.48 | | |
| | | | | | **20.86** | **3.50** | **12.18** | **3.90** |
| Cl | 12.96 | 3.613 | 8.29 | 2.58 | 12.974 | 3.69 | | |
| | | | | | **15.03** | **3.73** | **9.38** | **2.95** |
| Br | 11.811 | 3.363 | 7.59 | 2.34 | 11.84 | 3.55 | | |
| | | | | | **13.10** | **3.70** | **8.40** | **2.62** |
| I | 10.448 | 3.063 | 6.75 | 2.06 | 10.45 | 3.21 | | |
| | | | | | **12.67** | **3.52** | **8.10** | **2.52** |
| H | | | | | 13.595 | 0.747 | | |
| | | | | | **13.595** | **0.747** | **7.17** | **2.21** |

[a] Roman type. [b] Boldface type. [c] Reference 5. [d] Reference 11. [e] Values in Pauling units, obtained by the equation $\chi_P = 0.336(\chi_M - 0.615)$. Values for hydrogen have been added for comparison.

It would be surprising if Mulliken values gave a significantly better fit than Pauling values in view of the generally good agreement between the two sets of values.[10,11] In fact, there is no significantly better agreement and the supposedly better correlation shown by the "Mulliken values" used by Clausen and Good is fortuitous.

Clausen and Good[5] and Herber and Cheng[9] made the error of using ground-state ionization energies rather than valence-state ionization energies. Briefly, the former measures the energy of forming the triplet state, $^3$P, for F$^+$ while the energy of interest for a fluorine atom bonding another atom is that for a singlet state, a suitably weighted mean of $^1$D and $^1$S.[12] Because of the higher spin-pairing energy of fluorine, electronegativities by the two methods differ more for it than for the larger halogens.[13]

Clausen and Good further erred in stating that "Pauling's electronegativities also give a value for fluorine which appears to be too high. . . caused by the failure . . . to account fully for the anomalous destabilization energy inherent in the formation of the fluoride ion."[14,15] Pauling's values were empirical values obtained directly from experimentally obtained bond energies If M–F bonds are consistently destabilized to the extent of *ca.* 25 kcal/mol as suggested by Politzer,[15] then all of

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(1) V. I. Goldanskii, *At. Energy Rev.*, **4**, 3 (1963).

(2) V. I. Goldanskii, E. F. Makarov, R. A. Stukan, T. N. Sumarokova, V. A. Trukhtanov, and V. V. Krapov, *Dokl. Akad. Nauk SSSR*, **156**, 400 (1964).

(3) M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, **26**, 915 (1964); V. I. Goldanskii and R. H. Herber, Ed., "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

(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) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(7) R. J. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, **7**, 1603 (1968).

(8) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935); W. Moffit, *Proc. Roy. Soc., Ser. A*, **202**, 548 (1950).

(9) H. S. Cheng and R. H. Herber, *Inorg. Chem.*, **9**, 1686 (1970).

(10) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

(11) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1963); J. Hinze, M. A. Whitehead, and H. H. Jaffé, *J. Amer. Chem. Soc.*, **85**, 148 (1963).

(12) See ref 10, pp 754–755, for a lucid discussion of the valence state and Mulliken electronegativities.

(13) Although the ground-state ionization potentials and electron affinities used by Clausen and Good[5] differ from those of Jaffé, *et al.*,[11] by an average of only 0.06 eV and from those of Pritchard and Skinner[10] by only 0.10 eV, their recomputed electronegativities differ by an average of 1.25 and 1.37 eV, respectively. The largest discrepancy between the electronegativities of Clausen and Good and those of earlier workers is 1.75–1.80 eV for fluorine (see Table I).

(14) At this point Clausen and Good referred to our ref **15**.

(15) P. Politzer, *J. Amer. Chem. Soc.*, **91**, 6235 (**1969**).

the ionic resonance energies that Pauling obtained for fluorine compounds would be 25 kcal/mol *less* than if this effect did not take place. Hence the computed differences between the electronegativity of fluorine and those of the remaining elements would also be *less*. It is thus possible to argue that the "theoretical" or "ideal" electronegativity of fluorine should be *higher* than Pauling's empirical value but not lower. As a matter of fact, the bond energy in gaseous $SnF_4$ corresponds to an electronegativity difference of 1.4 units in very good agreement with, and slightly *larger* than, the difference of 1.2 units on Pauling's scale.[16] The "failure" of the Pauling equation has been discussed elsewhere.[17] It was concluded that although there are some shortcomings the equation has a firm basis in terms of current electronegativity theory.

The resolution of the apparent anomaly of fluorine and the isomer shift of the hexafluorostannate(IV) ion can be provided by a simple calculation. Standard Mulliken–Jaffé electronegativity values[11,18,19] and complete equalization of electronegativity[19] are assumed as a first approximation although the qualitative results are indifferent to these assumptions. Calculations employing incomplete equalization[20] yield similar results.

The results of this calculation are shown in Figure 1. There is a good correlation ($r = 0.99$) between induced charge and the isomer shift for both the tetrahedral ($IS_{Td} = -3.68\delta_{Sn} - 0.03$) and the octahedral ($IS_{Oh} = -8.19\delta_{Sn} + 0.49$) species (where IS is the isomer shift in mm/sec relative to gray tin and $\delta_{Sn}$ is the estimated charge on tin). *Hexafluorostannate(IV) falls on the octahedral line* and its collinearity is *not* dependent upon any of our assumptions but is implicit in the two-parameter Mulliken–Jaffé electronegativity values. The better fit of the results of our calculations is a result of the fact that the isomer shift is dependent upon the s-electron density and the nucleus[21] and thus is related to the effective nuclear charge. Hence the parameter of primary interest is not the inherent electronegativity of the substituents but the *charge* which that electronegativity can induce on the tin atom. In a system of fixed electronegativities the induced charge is dependent only on the electronegativity difference,[7] but a two-parameter scale[12,19] takes into account the capacity for donation or acceptance of charge as well as the inherent tendency to donate or accept charge.[22] Fluorine differs from the remaining halogens in its reduced charge capacity ("polarizability"). The small fluorine atom cannot readily accept *large* amounts of charge. In this sense the interpretation of Politzer[15] is appropriate, but when the ionicity is low, the effect does not appear.[23]

Although the correlation between isomer shift and calculated charge (or electronegativity) is good and has been used to obtain group electronegativities,[4,9] we should like to point out that calculated charges (or electronegativities) are insufficient to account completely for isomer shifts. For example, as noted by Herber and Parisi,[24] the isomer shift for stannane, $-0.83$ mm/sec, does not fall on any of the correlation plots offered thus far, including our own. Organotin compounds offer similar problems. It would appear that $\pi$-bonding capabilities of the ligands may well be involved in the isomer shift. We are currently investigating the problem of correlating the organotin compounds.

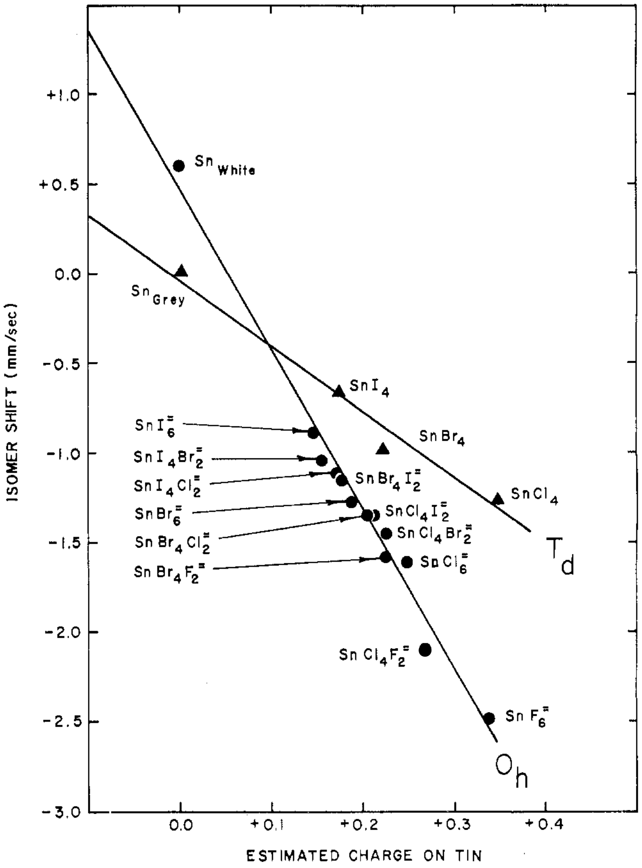

Figure 1.—Isomer shift as a function of estimated charge on the tin atom in tetrahedral and octahedral species.

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(16) Calculated by the geometric mean method using the following bond energies: Sn–Sn = 36, F–F = 37 kcal/mol (T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958) and Sn–F = 99 kcal/mol (R. C. Feber, Los Alamos Report LA-316A, 1965, available from the Clearinghouse for Federal Scientific and Technical Information, U. S. Department of Commerce, Springfield, Va.). The agreement is especially good if it is remembered that Pauling did not have these data available to him and assigned the values indirectly from other data.

(17) R. S. Evans and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **32**, 373, 383, 777 (1970).

(18) These values are given in a form more suitable for computation in ref 19. The assumed hybridizations are as follows: halogens, p; octahedral tin, $sp^3d^2$; tetrahedral tin, 0.67 $sp^3$–0.33$sd^3$. The d-orbital electronegativity of tin is taken as $2.7 + 2.0\delta_{Sn}$ (where $\delta_{Sn}$ is the charge on tin).

(19) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965), and references therein.

(20) J. E. Huheey, *J. Org. Chem.*, **31**, 2635 (1966).

(21) V. I. Goldanskii and E. F. Makarov in "Chemical Applications of Mössbauer Spectroscopy," V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968.

(22) For a related manifestation of this effect see W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962); J. E. Huheey, *J. Org. Chem.*, **36**, 204 (1971).

(23) See ref 17 for discussions of this effect and partial charges in various halides.

(24) R. H. Herber and G. I. Parisi, *Inorg. Chem.*, **5**, 769 (1966).

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