Inorganica Chimica Acta, 13 (1975) L11 - L12

Photoelectron Spectra and the Question of pπ → dπ Interactions in Silane and Germanes

C. GLIDEWELL

Department of Chemistry, University of St. Andrews, Fife, Scotland, U.K.

(Received January 15, 1975)

In the photoelectron spectra of a number of methyl, silyl (SiH_3–) and germyl (GeH_3–) derivatives of the form MH_3X [1,2] (M = C, Si, Ge; X = Cl, Br, I), $(MH_3)_2Y$ [3] (Y = O, S, Se, Te), $(MH_3)_3Z$ [4] (Z = N, P, As) and MH_3Q [5] (Q = NCO, NCS, NNN), the first ionisation potentials, corresponding to ionisation in each case of an essentially non-bonding electron, either from the atom X, Y or Z or from the α-nitrogen atom of Q, are found always to increase in the order $CH_3 < GeH_3 < SiH_3$ (see Table), and this has generally been interpreted as evidence for the occurrence of pπ → dπ bonding, involving the unshared pairs of electrons on X, Y, Z or Q: and 3dπ or 4dπ orbitals on silicon or germanium respectively: such π-interactions are thereby eliminated[6] as a principal determinant of the unusual geometry found in the silyl and germyl derivatives of nitrogen and oxygen, but not in the derivatives of the heavier elements of Groups V and VI.

The purpose of the present note is to make two points. The first is general: it is assumed[1-5] that the ionisation potentials of the methyl compounds are normal and may consequently be taken as a standard against which to compare the ionisation potentials of the silyl and germyl compounds, so that any apparent discrepancy requires interpretation in terms of the atomic properties of silicon and germanium. However one of the principal lessons of comparative inorganic chemistry is that if any period of elements can be said to show atypical properties, that period is the first one (Li → F); so that the methyl compounds in this case may not represent an ideal standard.

The second point is specific, namely that the corresponding ionisation potentials for the hydride species HX, H_2Y, H_3Z and HQ are higher even than those of the silyl species, and that introduction of the group CF_3– generally raises the first (lone-pair) ionisation potential still further, thus: $CH_3 < GeH_3 < SiH_3 < H < CF_3$ (see Table). There is ample evidence[14] to indicate that relative to hydrogen, the CH_3– group is a net electron donor and the CF_3– group is a net electron acceptor: this accords with the ordering of the ionisation potentials in these compounds $CH_3 < H < CF_3$. The implication of the ionisation potential data is therefore that far from being electron acceptors by means of pπ → dπ interactions, as suggested[1-5], the SiH_3– and GeH_3– groups are in fact net electron donors relative to hydrogen, albeit less effective than CH_3–.

TABLE. Lone Pair Ionisation Potentials (eV) for RX, R_2Y, R_3Z and RQ[a,b]

X	CH_3	SiH_3	GeH_3	H	CF_3
Cl	11.28	11.61	11.30	12.79[d]	12.92[j]
Br	10.69[c]	11.03[c]	10.72[c]	11.85[d]	12.3[k]
I	9.85[c]	10.05[c]	9.87[c]	10.7[d]	10.4[j]
Y					
O	10.04	11.17	10.40	12.61[e]	
S	8.71	9.70	9.25	10.47[e]	
Se	8.40	9.18	8.84	9.88[f]	
Te	7.89	8.63	8.34		
Z					
N	8.5	9.7	9.2	10.85[g]	
P	8.6	9.3	9.0	9.9[h]	11.3[i]
As	8.3[i]	9.0		10.6[i]	11.0[i]
Q					
NCO	10.67	11.10	10.76	11.62	
NCS	9.37	9.54	9.14	9.94	
NNN	9.81	10.33	10.01	10.72	

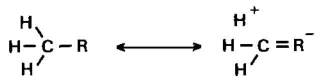
[a] R = H, CH_3, SiH_3, GeH_3 or CF_3. [b] Values from refs. 1 - 5, except where otherwise stated. [c] Mean of two Jahn–Teller components. [d] Ref. 7; mean of ionisation potentials to $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. [e] Ref. 8. [f] Ref. 9. [g] Ref. 10. [h] Ref. 7. [i] Ref. 11. [j] Ref. 12. [k] Ref. 13.

The weaker binding (lower ionisation potential) of the lone-pair electrons in the MH_3– species compared with the H– species implies either a lower effective nuclear charge at the atom X, Y or Z, or a π-perturbation caused by mixing of the pπ lone-pair orbital with another, more tightly-bound, orbital of π symmetry. No such π-interactions can occur with hydrogen as substituent, (unless orbitals such as H(2p) are considered important), and this is reflected in the similarity of the first ionisation potentials of these species to those of the atoms[15], for example; Cl, 13.01 eV; Br, 11.84

eV; I, 10.45 eV: it is for this reason that hydrogen (found thus to be electronically approximately neutral) rather than methyl (known to be an electron donor) derivatives should in this context be chosen as the standard compounds with which others are to be compared.

If the principal cause of the order of the ionisation potentials found for the MH_3- species is the variation of the effective nuclear charge at the atom X, Y or Z, this implies an order of electronegativity coefficients $X_H > X_{SiH_3} > X_{GeH_3} > X_{CH_3}$: no set of experimental coefficients derived from Pauling's thermochemical equation[16], or from Mulliken's definition[17], or from nmr data[18] lies in this order; in particular $X_{CH_3} > X_H$ on all scales. It is concluded that a π-perturbation is operative.

The electron donor ability of the methyl group in CH_3R is generally supposed to operate via a π-overlap involving an e-type π combination of the hydrogen orbitals, a pπ orbital on carbon and a pπ orbital on atom R: in valence-bond terms structures such as



are important. The present suggestion is that such a process is less important in SiH_3- and GeH_3- species, since whereas the CH bond is polarised $C^{\delta-}–H^{\delta+}$, the SiH and GeH bonds[19] are polarised $Si^{\delta+}–H^{\delta-}$ and $Ge^{\delta+}–H^{\delta-}$, so that the feebler electron donor ability of the silyl and germyl groups may be at least partly understood.

References

1 S. Cradock and R. A. Whiteford, *Trans. Faraday Soc., 67,* 3425 (1971).

2 D. C. Frost, F. G. Herring, A. Katrib, R. A. N. McLean, J. E. Drake and N. P. C. Westwood, *Chem. Phys. Letters, 10,* 347 (1971).

3 S. Cradock and R. A. Whiteford, *J. Chem. Soc. (Faraday II),* 281 (1972).

4 S. Cradock, E. A. V. Ebsworth, W. J. Savage and R. A. Whiteford, *J. Chem. Soc. (Faraday II),* 934 (1972).

5 S. Cradock, E. A. V. Ebsworth and J. D. Murdoch, *J. Chem. Soc. (Faraday II),* 86 (1972).

6 C. Glidewell, *Inorg. Chim. Acta Revs., 7,* 69 (1973).

7 D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley–Interscience, London (1970).

8 W. C. Price, *J. Chem. Phys., 4,* 147 (1936).

9 W. C. Price, J. P. Teegan and A. D. Walsh, *Proc. Roy. Soc. (A), 201,* 600 (1950).

10 B. Brehm and E. von Puttkamer, *Int. Conf. Mass. Spectr.,* Berlin (1967), cited in ref. 7).

11 W. R. Cullen and D. Frost, *Canad. J. Chem., 40,* 390 (1962).

12 R. Bralsford, P. V. Harris and W. C. Price, *Proc. Roy. Soc. (A), 258,* 459 (1960).

13 V. H. Dibeler, R. M. Reese and F. L. Mohler, *J. Res. Nat. Bur. Stand., 57,* 113 (1956).

14 See, for example, E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York (1959) and references therein.

15 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev and Y. L. Frankevich, "Bond Energies, Ionisation Potentials and Electron Affinities", Arnold, London (1966).

16 L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York (1960).

17 R. S. Mulliken, *J. Chem. Phys., 2,* 782 (1934); *3,* 573 (1935).

18 B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc., 77,* 3977 (1955).

19 A. P. Altshuller and L. Rosenblum, *J. Am. Chem. Soc., 77,* 272 (1955).