Catenates of the Group IV Elements. Correlation of σ Electron Energies

Colin G. Pitt, Maurice M. Bursey, and Peter F. Rogerson[1]

Contribution from the Chemistry and Life Sciences Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709, and the Venable Chemical Laboratory, University of North Carolina, Chapel Hill, North Carolina 27514. Received June 30, 1969

Abstract: The electron impact ionization potentials of the catenates of the group IV elements, $R(R_2M)_nR$ where R = alkyl and M = Si, Ge, Sn, have been determined and compared with those of the analogous alkanes $H(CH_2)_nH$. It is shown that there is a systematic decrease in the ionization potential as the chain length (n) increases and as group IV is descended. The variation of the ionization potential with chain length is discussed in terms of the various semiempirical treatments of saturated molecules. The trends in the electronic absorption spectra of the group IV catenates are shown to be directly related to the ionization potential and, as a consequence of Koopmans' theorem, to the ground state of the molecules.

Compounds which contain metal–metal bonds have attracted increasing attention during the past decade.[2] Understandably, physicochemical studies of this interesting class of compounds have lagged behind synthetic studies, and little systematic information is available on the trends in the properties which are to be expected as the metal is varied. The authors have been particularly interested in the electronic properties of the homonuclear metal–metal bond formed by main group elements and have turned to the derivatives of the group IV elements in order to determine how the properties may vary within a specific group. The catenates of carbon (*i.e.*, alkanes) have, of course, already been very extensively studied and represent an established model for comparison with the catenates of the more electropositive group IV elements. This paper will first report and discuss the trends in the electron impact ionization potentials of the catenates of this group, and will then show how the results are relevant to the controversial[3] question of the origin of the electronic spectra of these compounds.

Experimental Section

The ionization potentials were measured using a Hitachi RMU 6E mass spectrometer, modified by the incorporation of a digital voltmeter readable to ± 0.01 volt (United Systems Corporation, Dayton, Ohio), with reduced trap current (*ca.* 2 μA) and repeller voltage (<0.5 V). As a result of extensive experimentation with the semilogarithmic method,[4] we found it to be no more desirable than the single-point method of Kiser (that is, his energy compensation technique)[5] with respect to the production of reproducible data. A modification of the energy compensation technique was therefore employed.

As a precaution, it was first observed that for both standards and unknowns, the semilogarithmic ionization efficiency curve was linear at the 1% intensity value; in general it was near the higher end of the linear portion of the curve. The 1% value then served for the single point of the energy compensation technique. Xenon was used as a calibration standard; but since there was no certainty of the linearity of the voltage scale below the IP of xenon, two auxiliary standards, benzene and anthracene, whose ionization potentials bracket most of those determined in this study, were also used.

Since electron-impact data are being reported, it seemed more appropriate to calibrate the data for unknowns using the electron impact-IP of the standards, rather than the adiabatic values. Hence the average electron impact values which were used, obtained from compilations of recent values,[6] were as follows: Xe, 12.12; C_6H_6, 9.23; and $C_{14}H_{10}$, 7.41 eV.

Data were collected on different days, always in groups of three runs, each with four data points, *i.e.*, Xe, $C_{14}H_{10}$, C_6H_6, and the unknown. The three sets of data for knowns were used to find the best slope of a correlation line, and this correlation line of fixed slope was then applied to each set of data individually. The value of the unknown IP was then determined for each set of data. This method of correlation, while unusual, did not give significantly different results from a least-squares treatment for interpolated unknowns. Furthermore, it did avoid wide fluctuations in results for extrapolated unknowns which occurred when a deviation was found for one terminal standard IP. Our results, to repeat, are mostly interpolative, with only a few short extrapolations.

In general, six runs were made for each compound, with some data obtained on different days. The error figures quoted are the standard deviations of all determinations, that is, figures of precision. They do not represent the authors opinion of accuracy, which is 0.1–0.2 eV for the electron-impact method. This error applies to the absolute scale. For intercomparison of these data, the relative accuracy seems to be greater (*ca.* 0.03 eV, or the sum of the precision values for two compounds); this method seems particularly good for comparison of members of a closely related series of compounds.

Compounds used in this investigation were prepared by standard literature procedures.[7]

Results and Discussion

Because of their synthetic availability, the peralkylated catenates of silicon, germanium, and tin, *i.e.*, $Me(MMe_2)_nMe$, have been compared with the alkanes $H(CH_2)_nH$. In terms of σ–σ interactions, which play a critical role in determining IP's, this is a reasonable comparison. That is because interaction of the σ electrons of the substituent with the σ electrons of the chain will be comparable in all of these series and, to a first approximation, negligible when compared with σ–σ interaction of electrons associated only with the chain. If the comparison were made to $Me(CMe_2)_nMe$, the σ interactions involving the substituent electrons in this series would be of comparable magnitude to those involving the chain, and so not negligible.

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Table I

Compound	Obsd IP, eV	Calcd IP, GO method[a]	Calcd IP, "C" method[b]	λ_{max}, nm[c]	$h\nu$, eV
Me(Me₂Si)₂Me	8.00 ± 0.01	(8.00)	8.22	193.5[c]	6.41
Me(Me₂Si)₃Me	7.53 ± 0.01	7.53	7.55	216.3[c]	5.73
Me(Me₂Si)₄Me	7.29 ± 0.01	(7.29)	7.26	235.0	5.28
Me(Me₂Si)₅Me	7.11 ± 0.01	7.16	7.10	250.0	4.96
Me(Me₂Si)₆Me	7.02 ± 0.02	7.08	7.00	260.0	4.77
Me(Me₂Si)₈Me	6.82 ± 0.02	6.99	6.90	272.5	4.55
(Me₂Si)₅	7.18 ± 0.01	7.28	7.17	272, 261	4.56, 4.75
(Me₂Si)₆	7.29 ± 0.01	6.85	6.77	255, 232	4.86, 5.34
(Me₂Si)₇	7.39 ± 0.01	6.99		242, 217	5.12, 5.71
MeSi(SiMe₃)₃	7.41 ± 0.01	7.16		<200	<6.2
Si(SiMe₃)₄	7.41 ± 0.01	6.85		<200	<6.2
n-Me₇Si₃CH₂SiMe₃	7.38 ± 0.01			217.7[e]	5.70
Me(Me₂Ge)₂Me	7.76 ± 0.01			190.0	6.53
Et(Et₂Ge)₂Et	7.48 ± 0.01[d]			202[e]	6.14
Me(Me₂Sn)₂Me	7.42 ± 0.02			210.0	5.90
Et(Et₂Sn)₂Et	6.60 ± 0.02[d]			232[f]	5.34

[a] Group orbital method. [b] Sandorfy C approximation. [c] Values from ref 26. [d] Average of only three determinations. [e] Reference 20. [f] Reported as shoulder.

The IP's of the group IV catenates examined in this study are compiled in Table I. Of the silanes, only hexamethyldisilane has been studied previously. Lappert, et al.,[8] report a value of 8.35 ± 0.12 eV, in reasonable agreement with the figure given here. A value of 8.79 ± 0.08 eV, determined by the retarding potential difference technique, has also been reported[9] for this compound but might be questioned.[10] DeRidder and Dijkstra[11] have determined the IP's of hexamethyl- and hexaethyldigermane, but their use of the linear extrapolation method negates any comparison with the values in this paper. Regardless of the absolute values, the internal consistency of the present results is implicit in the fact that the plot of the IP'S of polysilanes vs. Honig's[12] values of the corresponding alkanes is linear.

The linearity of this plot of the IP's of the silanes and alkanes, which may be expressed as $IP_{Si} = 0.6735IP_C + 0.00$, simplifies the analysis of the trend in IP's listed in Table I, for it means that the various semiempirical treatments which have been used to discuss the properties of the alkanes may be applied with equal success to the silanes. One of the most simple of these treatments is the group orbital method,[13] which involves the solution of the secular equation (1), using parameters of the groups $-CH_2-$ or $-SiMe_2-$ rather than the individual atoms. Only nearest neighbor interactions are considered ($e_{rs} = 0$ when $r \neq s, s + 1$) and the method is analogous to the Hückel LCAO treatment of π systems.

$$|e_{rs} - E\delta_{rs}| = 0 \qquad (1)$$

Deriving the values $e_{rr} = 9.15$ and $e_{rs} = 1.15$ from the experimental IP's of the disilane and tetrasilane, the trend in the IP's of the other silanes can be approximated, as shown in Table I. The above values of e_{rr} and e_{rs} are to be compared with Franklin's numbers,[13] 13.31 and

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1.55, respectively, for the alkanes, the difference in the value of e_{rr} being a reflection of the electropositivity of the two series.

Treatments[14] which are based on the Sandorfy "C" type of approximation represent a slightly more sophisticated theoretical model. In this approximation,[15] which also involves solution of the secular equation (1), interactions of the substituents and second and higher order interactions of the orbitals of the chain are ignored. However, in addition to the resonance integral (β_{vic}) of overlapping atomic orbitals, a second, smaller resonance integral (β_{gem}) involving the orbitals on the same catenate atom is introduced (Figure 1). It is this second parameter which reproduces the limited delocalization of σ electrons, and the slope (0.67) of the correlation $IP_{Si} = 0.6735IP_C$ represents the ratio of the values of β_{gem} in the alkane and silane series. The slightly lower value of β_{gem} for the silanes is consistent with the idea that this term will decrease as the atomic orbitals become more diffuse, although the dissimilar substituents complicate the comparison. The values of α, β_{vic}, and β_{gem} for the silanes were derived, as described by Fukui, et al.,[14] for the alkanes, by finding the best fit of the experimental IP's to the solutions of the secular equation which incorporates α, β_{vic}, and β_{gem}. The values of α, β_{vic}, and β_{gem} for the silanes are -3.94, -4.28, and -1.48 eV, compared with the corresponding values, -5.850, -6.364, and -2.205 eV, derived by Fukui, et al.,[14] for the alkanes. The theoretical IP's of the silanes calculated using these parameters are included in Table I.

In the more sophisticated quantum mechanical treatments of the alkanes, such as the equivalent orbital method of Hall and Lennard-Jones,[16] and the Sandorfy "H" method,[15] interactions involving the substituents and nonnearest neighbor interactions are also included in the secular equation. However, this introduces an ambiguity, for it is found that the C–H and C–C orbitals in alkanes are of similar energy, and there is still some disagreement as to which of these orbitals is involved in the ionization process. For example, in the case of

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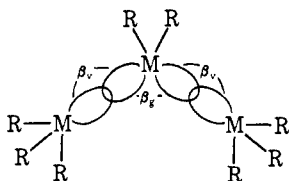(16) G. G. Hall, Proc. Roy. Soc., A, 205, 541 (1951); J. E. Lennard-Jones and G. G. Hall, ibid., 213, 102 (1952).

Figure 1.

ethane, both the a_{1g} orbital (largely C–C)[16,17] and the e_g orbital (C–H)[18] have been implicated. A comparable theoretical treatment of the silanes has not been attempted, but fortunately the experimental values of the IP's allow some empirical conclusions to be drawn. For example, the IP of hexamethyldisilane (8.00 eV) is much lower than that of tetramethylsilane (9.53 eV),[19] and this large decrease can hardly be explained by the effect of the second electropositive silicon atom on the Si–C or C–H σ electrons, for the IP's of compounds which contain the SiCH$_2$Si grouping are >9.2 eV.[20] This conclusion is substantiated by the unexceptional IP's of the branched polysilanes and n-Me$_7$-Si$_3$CH$_2$SiMe$_3$ (see Table I), and the electronic charge resulting from ionization must logically be associated primarily with the more electropositive Si–Si bond.

The IP's of the first members ($n = 2$) of the group IV catenates provide further information about the electronic structure. The IP's in the series Me$_6$M$_2$, M = Si, Ge, and Sn, are essentially the same as those of the parent metal (C, 11.26 eV; Si, 8.15 eV; Ge, 7.88 eV; Sn, 7.34 eV).[21] One would expect that electrons in a σ bond formed from the atomic orbitals of the metal would be more stable than the electrons originally associated with the free metal. The correspondence between the IP's of the compound and the parent metal means that the electron cannot be lost from a molecular orbital which is totally σ_{M-M}, for it would then correspond to a nonbonding orbital. There must therefore be some contribution of the σ_{M-C} and σ_{C-H} orbitals to the highest occupied molecular orbital. The fact that the IP of ethane (11.65 eV) is appreciably greater than that of elemental carbon (11.25 eV) is presumably a reflection of the fact that mixing of the σ_{C-H} and σ_{C-C} electrons is less significant. The decrease (0.3 eV) in the IP of hexaethyldigermane relative to that of hexamethyldigermane is in accord with the above picture, although the decrease (0.8 eV) in the IP of hexaethyldistannane relative to hexamethyldistannane appears excessively large. Nmr studies[22] have suggested abnormally high p character in the tin–methyl bond of hexamethyldistannane, so there may be much greater mixing of the Sn–Sn and Sn–C orbitals relative to that in the lighter elements. Alternatively, Koopmans' theorem,[23] which has been suggested to fail in the case of

Figure 2. Plot of IP $vs.$ ν_{max} for homologous series of permethylated polysilanes, Me(Me$_2$Si)$_n$Me.

large polarizable systems,[24] may begin to deviate for the tin compounds.

From the general trend in the IP's of these catenates, it is not difficult to see why the oxidative stability should decrease from carbon to tin, to the extent that some polystannanes are pyrophoric.[25]

Relevance to the Electronic Absorption Spectra of Group IV Catenates. It has been observed[26] that catenates of the heavier group IV elements, R(R$_2$M)$_n$R where R = alkyl and M = Si, Ge, Sn, Pb, absorb in the ultraviolet and visible. Because σ electrons must be involved, and because catenates of carbon ($i.e.$, alkanes) do not absorb above 160 nm,[27] it has frequently been suggested that the low energy of these transitions is a consequence of the energetically accessible d orbitals in these heavier elements. The interaction of adjacent d orbitals along the chain, and the fact that d orbital utilization is more important for the heavier elements, may then be used to explain why the absorption is red-shifted as the chain length (n) is increased and as group IV is descended.

Alternatively, because the energy of an electronic transition reflects the properties of the ground state as well as the excited state, it is necessary to consider whether the spectral trends may derive from the contribution of the ground state σ framework. It is now generally accepted that σ electrons are delocalized ($vide$ $supra$) rather than restricted to specific bonds.[28] The increasing delocalization of the σ electrons, as the chain length of the above catenates is increased, will result in destabilization of the highest occupied molecular orbital and account for a red shift of the electronic transitions. The increase in electropositivity in the series C, Si, Ge,

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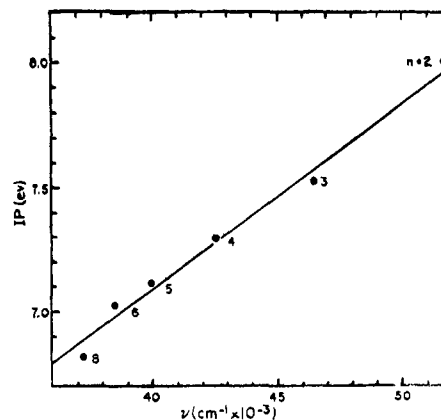
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Sn, and Pb, will also result in a higher energy σ framework and explain the observed red shift associated with the heavier metals.

Since the ionization potential may be equated with the energy of the highest occupied molecular orbital in the molecule,[23] the results summarized in Table I may be used to evaluate the relative merits of these two independent explanations of the electronic spectral shifts of the catenates. First, note that the IP's of the polysilanes fall in the range 8.0–6.8 eV, and these lower values, when compared with the IP's of the corresponding alkanes (11.7–10.2 eV), are more than sufficient to explain the large red shift (~3 eV) in the absorption maxima of the silanes. Also the dependence of the absorption maxima on the chain length of the catenate is identical with the dependence shown by the IP's. This is clearly illustrated graphically by the plot of ν_{Si_n} vs. IP_{Si_n} (Figure 2), and this excellent linear correlation strongly suggests that the energy of the electronic transition is partly determined by the IP, that is the energy of the silicon–silicon framework. The same conclusion is supported by the fact that the IP's of the cyclic polysilanes, $(Me_2Si)_n$, $n = 5, 6, 7$, which must depend on a combination of electronic and steric (ring strain) factors, are able to account for the anomalous trend[29] in the absorption maxima of these compounds. The IP's of the branched polysilanes appear to be normal, so the failure of these compounds to absorb above 200 nm remains an enigma.

The slope of the correlation line in Figure 2 indicates that the ground state is responsible for only 60% of the total change in energy of the electronic transition as the chain length of the series $Me(SiMe_2)_nMe$ increases. So while it is perhaps hazardous[30] to compare parameters derived from absorption spectra with parameters derived from IP measurements, this means that in terms of the Sandorfy "C" approximation, the ground state geminal resonance integral and the corresponding excited state parameter are of similar magnitude. Ramsey[31] has pointed out that, for alkanes, the spectral shifts can be accounted for entirely by the changes in the ground state energy, so there appears to be a difference in the nature of the excited states of the two series.

It is premature to comment on the spectral properties of the polygermanes and polystannanes, with only the IP's of the first member of each series known. It will simply be noted that the absorption maxima of the series of permethylated germanes and permethylated silanes are virtually identical,[26e] yet the IP of the digermane is 0.5 eV lower than that of the disilane.

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