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Trends in ionization energies for group 14 catenates and influence of substituent nature on them

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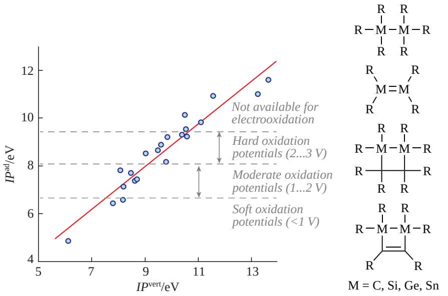
Adiabatic ionization energies for a series of acyclic and cyclic compounds containing M–M and M=M (M = C, Si, Ge, and Sn) bonds were calculated using DFT-TPSS/D3/def2-TZVPP and DFT-PBE0-DH/def2-TZVPP. Their changes when moving down group 14, as well as the influence of the substituent nature on them, were discussed.



Keywords: group 14 chemistry and reactivity, carbon family, catenation, ionization energy, radical cations.

The elements of group 14 (silicon, germanium, tin and lead) are known as carbon analogs. Despite the fact that they have a bright and diverse own chemistry coming from a more developed electron shell compared to carbon, the properties typical of carbon do indeed appear in them. For a century and a half, one of its main properties has been catenation, *i.e*., the tendency of carbon atoms to form bonds with each other. It is not typical for most other elements of the Periodic table, but it is quite characteristic of carbon analogs. The latter, however, differ, in particular, by the presence of σ-conjugation[1] in them, which makes polysilanes and polygermanes promising materials, for example, for use in microelectronics.[2] At the same time, this application is somewhat limited by the relatively greater vulnerability of Si–Si bonds to oxidation, compared to the C–C bond. However, the same property allows us to consider catenates of carbon analogs as promising compounds participating in oxidative addition and insertion of small molecules, for example, oxygen,[3] olefins,[4] hydrogen[5] and CO_2.[6] Such catenanes may also be available and highly active precursors of silyl radicals[7] and their heavier analogs, as well as cations, including silyl ones. The chemistry of silyl cations as highly active Lewis acids is currently intensively developed in the field of both the synthesis of organosilicon compounds[8] and the creation of promising catalysts.[9]

The basic quantitative parameter that determines the relative thermodynamic ease or difficulty of the oxidation of a compound is the ionization energy (potential) (IP).[10] The development of electron impact mass spectrometry, photoelectron spectroscopy, *etc*., in the last 70 years has made it possible to obtain IP values for a vast number of organic and organoelement compounds. However, IP values are largely limited to compounds with a relatively small molecular weight. In addition, at present, sufficiently accurate and reliable results can be obtained by calculation methods.[11] In our opinion, it would be interesting to establish how the oxidizability of the catenates changes in group 14 from top to bottom, depending on the substituent nature as well. Despite the available information, it is impossible to do this in full relying only on literature data. This communication is devoted to this problem.

Table 1 shows the adiabatic ionization potentials obtained using DFT-TPSS/D3/def2-TZVPP[31–38] for a series of derivatives of ethane **1**–**7**, ethylene **8**–**14**, cyclobutane **15**–**19** and cyclobutene **20**–**24** structures containing various substituents, along with their silicon, germanium and tin analogs. The IPs were determined as the difference between the free energies of the neutral and radical cation forms of the optimized structure of the compounds (see Online Supplementary Materials). The table also contains the known values of experimentally obtained vertical energies for some particular compounds. These two data sets are compared graphically in Figure 1. Despite the fact that in general one cannot expect a certain quantitative dependence between them (the electron transfer is accompanied by a

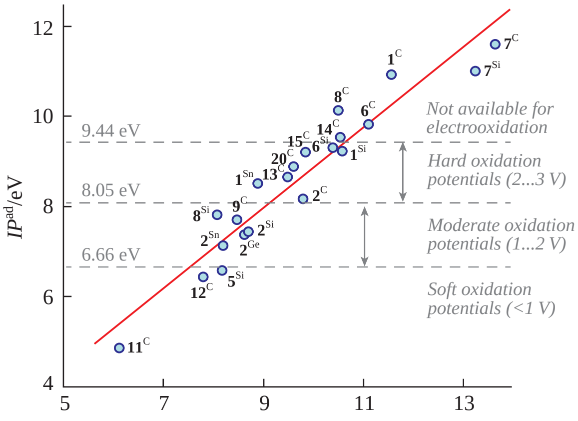
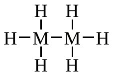
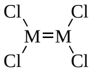
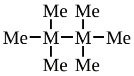
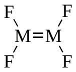
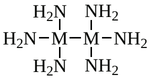
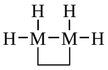
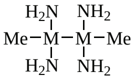
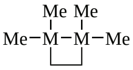
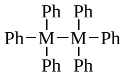
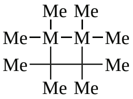
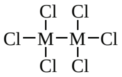
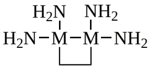
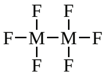
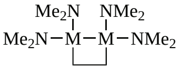
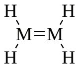
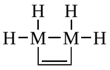
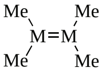
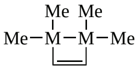
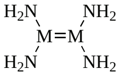
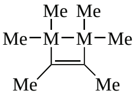
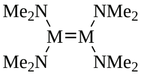
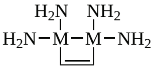
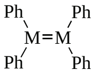
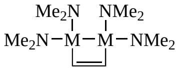


Figure 1 Correlation between the calculated adiabatic ionization energies and the vertical values available from the literature (see Table 1). The grey dashed lines show oxidation potentials *vs*. Ag/Ag^+ in MeCN estimated using the equation $IP^{ad} = 1.39E_p^{ox} + 5.27$ (see ref. 39).

Table 1 Adiabatic ionization energies (eV) of model compounds **1**–**24** obtained using DFT-TPSS/D3/def2-TZVPP. The experimental values of the vertical energies available from the literature are given in parentheses.

Compound		M				Compound		M			
		C	Si	Ge	Sn			C	Si	Ge	Sn
1		10.82 (11.56)[12]	9.28 (10.53)[13]	9.09	8.52 (9.00)[14]	**13**		8.66 (9.51)[24]	7.84	8.70	8.85
2		8.14 (9.80)[17]	7.44 (8.68)[18]	7.39 (8.59)[19]	7.16 (8.20)[18]	**14**		9.49 (10.52)[28]	8.65	9.84	9.80
3		7.04	6.58	6.93	6.99	**15**		9.19 (9.82)[29]	8.25	8.11	7.70
4		6.12	6.54	6.68	6.74	**16**		7.79	7.17	7.07	6.87
5		–[a]	6.60 (8.16)[22]	6.60	6.53	**17**		7.63	7.03	6.92	6.41
6		9.83 (11.10)[24]	9.34 (10.40)[25]	9.56	9.52	**18**		5.52	6.43	6.49	6.56
7		11.57 (13.60)[26]	10.99 (13.20)[27]	11.46	11.18	**19**		4.99	5.93	6.02	6.03
8		10.12 (10.51)[15]	7.80 (8.09)[16]	7.77	7.50	**20**		8.89 (9.59)[30]	8.59	8.40	7.95
9		7.68 (8.46)[20]	6.23	6.38	6.42	**21**		8.35	7.38	7.29	7.03
10		5.68	5.75	–[b]	–[b]	**22**		7.54	7.17	7.06	6.82
11		4.87 (6.13)[21]	5.30	–[b]	–[b]	**23**		4.09	6.58	6.65	6.73
12		6.42 (7.80)[23]	5.78	5.90	6.11	**24**		3.14	6.08	6.15	6.03

[a] The molecule breaks down into radicals $Ph_3C^{\bullet}$. [b] The structure is unstable.

reorganization of the resulting radical cation, and the latter contributes to the adiabatic energy and does not affect the vertical one), there is a correlation in the presented Figure. It can also be noted that the obtained values of the adiabatic potentials are naturally slightly lower than the vertical values, which is associated with reorganization.[39] In addition, IPs of these compounds were calculated using the PBE0-DH functional (see Online Supplementary Materials); however, the correlation was not fundamentally improved, and the values obtained using the two functionals turned out to be quite close.

It has recently been shown that the adiabatic ionization energies of permethylated germanium catenates calculated using this approach correlated well with the experimental oxidation peak potentials obtained (in the range of 1.0–2.7 V) in acetonitrile using the voltammetry method with the dependence $IP^{\mathrm{ad}} = 1.39\,E_{\mathrm{p}}^{\mathrm{ox}} + 5.27$ (potentials *vs*. Ag/Ag^+).[39] Figure 1 shows the levels of adiabatic energies of 6.66, 8.05 and 9.44 eV corresponding to the oxidation potentials of 1, 2 and 3 V obtained according to this equation. In the context of discussion, this may be illustrative and important from a practical point of view. First of all, compounds with oxidation potentials higher than 3 V are unavailable for electrochemical oxidation[40] (or rather, require special conditions, such as working in liquid sulfur dioxide[41]). The 2–3 V oxidation range may be called rather hard; compounds oxidizing in this range are relatively weak electron donors. Quantitative results obtained using quantum chemical and electrochemical methods are qualitatively transferred to practically significant chemical processes in which the oxidation of a compound plays a key role. As an example, in the potential range of 0.5–1.5 V biological and technical antioxidants are oxidized.[42] This range contains also analogs of carbenes[43] considered as potential participants in oxidative addition,[44,45] common oxidation mediators such as nitroxide radicals,[46] transition metals,[47] *etc*. Thus, the proposed qualitative levels may be considered when discussing the obtained values of ionization energies in the context of ‘easy’ or ‘difficult’ oxidation of compounds.

As can be seen from Table 1, the simplest group 14 catenates **1** (ethane, disilane, digermane and distannane) are characterized by high ($\mathbf{1}^{\mathrm{Si}}$, $\mathbf{1}^{\mathrm{Ge}}$, $\mathbf{1}^{\mathrm{Sn}}$) or very high ($\mathbf{1}^{\mathrm{C}}$) ionization energies. As expected, this parameter is the highest for ethane and approaches 11 eV. On going to silicon, the energy drops sharply, by more than one and a half eV (down to 9.28 eV). For digermane, it continues to decrease, but by a sharply smaller value, less than

0.2 eV (down to 9.09 eV); and again sharply, although not as much as in the case of the C→Si transition, the energy decreases on going to tin (down to 8.52 eV). The same trend persists on going to permethylated analogs **2**, although it becomes smoother (the total change from C to Sn is about 1 eV instead of ~2.5 eV). The IP values for series **2** are sharply smaller than those for series **1**, and they are in the range of moderate energies (7–8 eV). The appearance of substituents that are donors of an electron pair, in particular nitrogen (**3–4**) or halogens (**6–7**), removes the general pattern of a decrease in ionization energies down group 14. Amino derivatives **3–4** are oxidized easily or very easily, while the presence of chlorine and especially fluorine leads to hard energies that are higher compared to those for analogs substituted with hydrogen (**1**) in all cases except for the pair **6**$^{\mathrm{C}}$/**1**$^{\mathrm{C}}$. In the case of hexaphenyl derivatives **5**, the **5**$^{\mathrm{C}}$ structure does not exist according to calculations, while **5**$^{\mathrm{Si}}$, **5**$^{\mathrm{Ge}}$ and **5**$^{\mathrm{Sn}}$ are characterized by similar ionization energies.

Compared to saturated derivatives **1**, ethylene and its analogs **8** are oxidized by about 1 eV more easily, but with a similar trend, namely, a sharp drop in ionization energies on going from C to Si, weak from Si to Ge, and more pronounced from Ge to Sn. In this case, the appearance of methyl groups (**9**) as substituents, as in case of **2**, sharply reduces the energies to moderate for **9**$^{\mathrm{C}}$ and soft, relatively close to each other, for **9**$^{\mathrm{Si}}$, **9**$^{\mathrm{Ge}}$ and **9**$^{\mathrm{Sn}}$. Amino (**10**) and dimethylamino groups (**11**) shift the oxidation to a very soft energy range (5–6 eV, see Figure 1), while the values down group 14 increase rather than decrease. The reason for this may be that in other compounds, the HOMO distribution area and the oxidation center are the M–M bond, which is affected by the substituent, while in amine derivatives, on the contrary, this centre is the substituent, which is affected by the M–M fragment. In the case of chlorine (**13**) and fluorine (**14**) derivatives, the energies are lower compared to **8** for **13**$^{\mathrm{C}}$ and **14**$^{\mathrm{C}}$, and are higher for the other pairs, while **13** is difficult to oxidize, and **14** is very difficult. Phenyl derivatives **12** are characterized by a sharp decrease in IP from C to Si, followed by a gradual increase in the Si→Ge→Sn series. All compounds of the **12** series are oxidized very easily.

Derivatives of cyclobutane and its analogs **15–19**, as well as cyclobutene and its analogs **20–24**, are of interest in that they are rather strained which potentially increases the reactivity of the M–M bond. In addition, the digermacyclobutene derivative is known to be capable of oxidative addition (insertion of oxygen into the Ge–Ge bond),[3] which is interesting from a practical point of view. As can be seen from Table 1, derivatives of cyclobutane and its analogs **15**, as well as their methylated forms **16–17** generally demonstrate the same behaviour as the acyclic forms: a sharp decrease in ionization energies from C to Si and a smoother decrease on going to tin. Methyl groups reduce energies down to very low ones. The electron pair donors, amino (**18**) and dimethylamino (**19**) groups, sharply decrease the energies compared to **15–17**; however, in the sequence from C to Sn, the corresponding compounds show an increase in IP, rather than a decrease (similar to **3–4** and **18–19**). In the whole, trends similar to those of **15–19** are observed for cyclobutene derivatives **20–24**.

It can be noted that in almost all cases both for M=M and M–M derivatives, pyramidization (trans-folding) can be found.[48–50] Most likely, it is associated with the second-order Jahn–Teller effect (pseudo-Jahn–Teller)[51] (see Online Supplementary Materials for details). With an increase in atomic mass, the effect is more pronounced.

In conclusion, we can say that the M–M bonds in catenates, consisting of two atoms from group 14, are themselves not extremely vulnerable to oxidation. However, by varying the substituents, this property can be effectively and significantly enhanced to practically accessible values or, conversely, stability can be increased.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.10.002.

References

1 A. Bande and J. Michl, *Chem. – Eur. J.*, 2009, **15**, 8504.
2 W. Fa and X. C. Zeng, *Chem. Commun.*, 2014, **50**, 9126.
3 W. Ando, M. Kako and T. Akasaka, *J. Chem. Soc., Chem. Commun.*, 1992, 458.
4 K. Mochida, C. Hodota and R. Hata, *Organometallics*, 1993, **12**, 586.
5 D. Wendel, T. Szilvási, C. Jandl, S. Inoue and B. Rieger, *J. Am. Chem. Soc.*, 2017, **139**, 9156.
6 N. Wiberg, W. Niedermayer, K. Polborn and P. Mayer, *Chem. – Eur. J.*, 2002, **8**, 2730.
7 J. Zeitouny and V. Jouikov, *Phys. Chem. Chem. Phys.*, 2009, **11**, 7161.
8 H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller and M. Oestreich, *Chem. Rev.*, 2021, **121**, 5889.
9 V. Ya. Lee, *Russ. Chem. Rev.*, 2019, **88**, 351.
10 C.-G. Zhan, J. A. Nichols and D. A. Dixon, *J. Phys. Chem. A*, 2003, **107**, 4184.
11 F. De Proft and P. Geerlings, *J. Chem. Phys.*, 1997, **106**, 3270.
12 G. Bieri, F. Burger, E. Heilbronner and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213.
13 H. Bock, W. Ensslin, F. Feher and R. Freund, *J. Am. Chem. Soc.*, 1976, **98**, 668.
14 F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, 1963, **2**, 50.
15 G. R. Branton, D. C. Frost, T. Makita, C. A. McDowell and I. A. Stenhouse, *J. Chem. Phys*., 1970, **52**, 802.
16 B. Ruscic and J. Berkowitz, *J. Chem. Phys.*, 1991, **95**, 2416.
17 L. Szepes, T. Korányi, G. Náray-Szabó, A. Modelli and G. Distefano, *J. Organomet. Chem.*, 1981, **217**, 35.
18 K. Mochida, S. Worley and J. Kochi, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3389.
19 V. F. Traven’, V. V. Redchenko, Y. Bartenev and B. I. Stepanov, *J. Gen. Chem. USSR*, 1982, **52**, 310 (*Zh. Obshch. Khim.*, 1982, **52**, 358).
20 P. D. Mollere, K. N. Houk, D. S. Bomse and T. H. Morton, *J. Am. Chem. Soc.*, 1976, **98**, 4732.
21 J. D. Bagnato, W. W. Shum, M. Strohmeier, D. M. Grant, A. M. Arif and J. S. Miller, *Angew. Chem., Int. Ed.*, 2006, **45**, 5322.
22 J. M. Gaidis, P. R. Briggs and T. W. Shannon, *J. Phys. Chem.*, 1971, **75**, 974.
23 G. Heublein and S. Spange, *J. Prakt. Chem.*, 1980, **322**, 949.
24 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Compounds*, Japan Scientific Societies Press, Tokyo, 1981.
25 P. Potzinger, A. Ritter and J. Krause, *Z. Naturforsch. A*, 1975, **30**, 347.
26 M. G. Inghram, G. R. Hanson and R. Stockbauer, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **33**, 253.
27 S. Cradock, E. A. V. Ebsworth and R. A. Whiteford, *J. Chem. Soc., Dalton Trans.*, 1973, **22**, 2401.
28 M. B. Robin, G. N. Taylor, N. A. Kuebler and R. D. Bach, *J. Org. Chem.*, 1973, **38**, 1049.
29 J. L. Holmes and F. P. Lossing, *Org. Mass Spectrom.*, 1991, **26**, 537.
30 K. B. Wiberg, G. B. Ellison, J. J. Wendoloski, C. R. Brundle and N. A. Kuebler, *J. Am. Chem. Soc.*, 1976, **98**, 7179.
31 J. P. Perdew, A. Ruzsinsky, G. I. Csonka, L. A. Constantin and J. Sun, *Phys. Rev. Lett.*, 2009, **103**, 026403.
32 J. P. Perdew, A. Ruzsinsky, G. I. Csonka, L. A. Constantin and J. Sun, *Phys. Rev. Lett.*, 2011, **106**, 179902.
33 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73.
34 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2018, **8**, e1327.
35 F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**, 224108.
36 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
37 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
38 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

39 M. P. Egorov, V. V. Jouikov, E. N. Nikolaevskaya and M. A. Syroeshkin, in *Organogermanium Compounds: Theory, Experiment, and Applications*, ed. V. Ya. Lee, Wiley, 2023, vol. 2, pp. 507–560.

40 O. R. Luca, J. L. Gustafson, S. M. Maddox, A. Q. Fenwick and D. C. Smith, *Org. Chem. Front.*, 2015, **2**, 823.

41 E. Garcia and A. J. Bard, *J. Electrochem. Soc.*, 1990, **137**, 2752.

42 A. Ya. Akyeva, A. V. Kansuzyan, K. S. Vukich, L. Kuhn, E. A. Saverina, M. E. Minyaev, V. M. Pechennikov, M. P. Egorov, I. V. Alabugin, S. V. Vorobyev and M. A. Syroeshkin, *J. Org. Chem.*, 2022, **87**, 5371.

43 K. V. Arsenyeva, K. I. Pashanova, O. Yu. Trofimova, I. V. Ershova, M. G. Chegerev, A. A. Starikova, A. V. Cherkasov, M. A. Syroeshkin, A. Ya. Kozmenkova and A. V. Piskunov, *New J. Chem.*, 2021, **45**, 11758.

44 A. Ya. Kozmenkova, V. A. Timofeeva, B. N. Mankaev, A. V. Lalov, E. A. Saverina, M. P. Egorov, S. S. Karlov and M. A. Syroeshkin, *Eur. J. Inorg. Chem.*, 2021, 2755.

45 P. G. Shangin, A. Ya. Akyeva, D. M. Vakhrusheva, M. E. Minyaev, B. N. Mankaev, V. A. Balycheva, A. V. Lalov, M. P. Egorov, S. S. Karlov and M. A. Syroeshkin, *Organometallics*, 2023, **42**, 2541.

46 P. A. Fedyushin, I. A. Zayakin, S. E. Tolstikov, A. V. Lalov, A. Ya. Akyeva, M. A. Syroeshkin, G. V. Romanenko, E. V. Tretyakov, M. P. Egorov and V. I. Ovcharenko, *Russ. Chem. Bull.*, 2022, **71**, 722.

47 A. B. Sheremetev, B. V. Lyalin, A. M. Kozeev, N. V. Palysaeva, M. I. Struchkova and K. Yu. Suponitsky, *RSC Adv.*, 2015, **5**, 37617.

48 P. P. Power, *Chem. Rev.*, 1999, **99**, 3463.

49 G. Bouhadir and D. Bourissou, *Chem. Soc. Rev.*, 2004, **33**, 210.

50 R. C. Fischer and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877.

51 H. B. Wedler, P. Wendelboe, D. J. Tantillo and P. P. Power, *Dalton Trans.*, 2020, **49**, 5175.

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