BOND DISSOCIATION ENERGIES IN ORGANOSILICON COMPOUNDS

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Introduction

All practising chemists need to know bond strengths. How else can they have any idea of the magnitude of the forces holding the atoms together in a molecule. Traditionally we express the strengths of these forces as energies, and additionally we focus strongly on *dissociation* energies because it is natural to ask "how much energy does it take to break a bond?" This has to be made clear at the outset because the term 'bond energy' without the qualifier 'dissociation' has the different meaning of an average. Not only is the meaning different but the values are often quite different, and this particularly in silicon chemistry.

The purpose of this brief account is to provide a summary of current values and to use these values to illustrate aspects of structure and bonding in organosilicon compounds and illuminate some of the synthetically most well known processes of organosilicon chemistry. It is not meant as an exhaustive review. For those who wish to delve more deeply, some useful references are offered at the end of the article.

Measurement

There are many methods of measuring bond dissociation energies. One of the most appealing, because it is the most direct, is somehow to dial in and record the exact amount of energy needed to break the bond and watch the molecule fall apart into two fragments. In principle this can be done nowadays by the technique of laser-induced photodissociation. But the circumstances need to be favourable (the molecule must absorb in the right energy region!) and only a few selected values have been obtained in this way (and none yet in organosilicon compounds). By and large the more successful methods are less direct. The bulk of them fall into the categories of kinetics, spectroscopy and ion threshold measurements. This scope of this article is too limited to offer experimental details of these methods except to say that they all have their particular advantages and difficulties. For each method there are usually explicit approximations made in working out the values and sometimes hidden assumptions, which can lead to conflicting results between different methods. Over the period of my own involvement in this field (some 30 years) there has been steady refinement starting from a situation where some values were uncertain to as much as ± 10 kcal mol^{-1} (and a lot not known at all) to one where many are now known to ± 1 kcal mol^{-1} and some to better than ± 0.5 kcal mol^{-1}. In 1966, for example, the average bond energy, $\overline{D}$(Si-H) = 77 kcal mol^{-1} was quoted for D(H$_3$Si-H) which is now known to have a value of 91.8 ± 0.5 kcal mol^{-1}.

It needs to be remembered, however, that the bulk of bond dissociation energy values come, not from measurement at all, but indirectly, by use of thermochemical cycles, *viz*,

$$D(\text{R-X}) = \Delta H_f^\circ(\text{R}) + \Delta H_f^\circ(\text{X}) - \Delta H_f^\circ(\text{RX})$$

where D(R-X) is the desired bond dissociation energy, ΔH_f^o(R) and ΔH_f^o(X) are the radical product enthalpies of formation and ΔH_f^o(RX) is the molecular enthalpy of formation. Thus the reliability of a particular dissociation energy depends on three ancillary ΔH_f^o values. The current data base of enthalpies of formation of organosilicon compounds and radicals is not particularly large and, most serious of all, the traditional method of measurement, calorimetry, has almost become extinct in the world's chemistry laboratories. In the light of this it is not surprising that *ab initio* theoretical chemistry has taken over the task of calculating bond dissociation energies in recent years. This development is in many ways exciting, but it carries the risk that, if theory outpaces experiment too far, we build our quantitative edifice on increasingly inadequate foundations.

Values

The currently best data for all Si-X bonds have undergone increases of *ca* +2 kcal mol^{-1} (and occasionally more) since my 1981 review. This is now quite well documented and arose because erroneous assumptions were made about the magnitude of activation energies for reactions of silyl radicals with HI and HBr (which have now been experimentally measured). Listed here are the data, based on experiment, for representative molecules containing Si-H, Si-C, Si-Si, Si-hal, Si-O, and Si-N bonds. Values from theory are generally in reasonable, if not precise, agreement, but are not given here.

(i) Si-H bonds

The data of table 1 show that Si-H bonds for which dissociation energies are known, lie in the range 84 - 104 kcal mol^{-1}. They are generally slightly weaker than the analogous C-H bonds in organic compounds (exceptions are $Ar_nH_{3-n}Si$-H bonds). Me-, Cl- and F-substituents are bond strengthening, while R_3Si- and Ph- are bond weakening. These effects can be understood in terms of electronegativity (the bond strengtheners) and the rather limited willingness of Si-centred radicals to delocalise with π-bonded systems (Ph substituent). Whereas Me substituents were originally thought to have no effect on Si-H bonds, they appear now to exert a small but significant strengthening. The same is true for all other Si-X bonds to a greater or lesser extent (see tables 2-4).

(ii) Si-C bonds

The data of table 2 gives values for Si-C bonds showing them to be as strong as, and in some cases stronger than, the analogous C-C bonds. It is interesting to note that Me substitution strengthens when at silicon but weakens when at carbon.

(iii) Si-Si bonds

The data of table 3 shows that Si-Si bonds are subject to the same influences as Si-H bonds. It was noted earlier that the silyl substituent weakening effect extends to elemental silicon itself where the average Si-Si bond energy is 54 kcal mol^{-1}. Si-Si bonds are definitely weaker than analogous C-C bonds.

(iv) Si-hal bonds

The data of table 4 shows the extraordinarily high strengths of Si-halogen bonds. The Si-F bond in SiF_4 is the strongest single bond known. The Si-hal and indeed the Si-O and Si-N bonds (see tables 5 and 6) are all much stronger than their carbon counterparts. This has been attributed to p_π- back bonding but other explanations are possible.

(v) Si-O and SiO-X bonds

The data of table 5 reveal the high strengths of Si-O bonds, but also the significant strengthening effect of an Me_3Si group as a substituent on oxygen. Thus the O-H bond in Me_3SiOH has a strength close to that in H_2O (119 kcal mol^{-1}) and much more than that in methanol (104 kcal mol^{-1}). Also the Si-O bond in $(Me_3Si)_2O$ is much stronger than that in Me_3SiOMe.

(vi) Si-N and SiN-X bonds

The data of table 6 show the same features as that of table 5, *viz* strong Si-N bonds and striking Me_3Si substituent strengthening effects. The N-H bond in $(Me_3Si)_2NH$ is actually stronger than that in NH_3!

(vii) π-bond energies

These are the values required for the notional process,

$$M{=}M \rightarrow \dot{M}\text{-}\dot{M}$$

where the product species is the supposed 1,2 diradical with non-interacting (orthogonal) singly occupied orbitals. The values come from heats of hydrogenation (estimated) and σ-bond dissociation energies. The reference values for purely organic species show that, approximately, the Si=Si and Si=C π-bonds have 40% and 60% of the strengths of the C=C π-bond, whereas the Si=O π-bond has 80% of that for C=O.

Applications

A number of the commercially significant processes (prototypes) of organosilicon chemistry are examined here from the point of view of their reaction enthalpies as approximately estimated from bond dissociation energies. While ΔH^o alone is not a sufficient criterion by which to determine the potential viability of a process, the majority of processes do have negative values (ie are exothermic).

(i) Hydrosilation

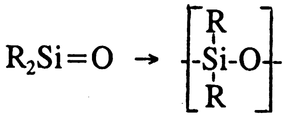
$$R_3SiH + C_2H_4 \rightarrow R_3SiCH_2CH_3$$

$$\begin{aligned}\Delta H^o &= D(\text{Si-H}) + D_\pi(\text{C=C}) - D(\text{Si-C}) - D(\text{C-H})\\ &= 94 + 65 - 92 - 100\end{aligned}$$

$$\underline{\Delta H^o = -33 \text{ kcal mol}^{-1}}$$

It is the turning of the C=C π-bond into σ-bonds (the essence of a polymerisation process) which makes this viable.

(ii) Polysiloxane creation from silanone monomer



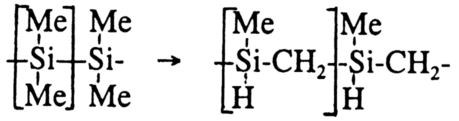
$$R_2Si{=}O \rightarrow \left[-\overset{R}{\underset{R}{Si}}-O-\right]$$

$$\begin{aligned}\Delta H^o &= D_\pi(Si{=}O) - D(Si\text{-}O)\\ &= \quad 61 \quad - \quad 136\end{aligned}$$

$$\underline{\Delta H^o = -75 \text{ kcal mol}^{-1}}$$

The driving force here is the significant advantage of the Si-O σ-bond over its π-bond. Interestingly, if we consider the more realistic model reaction starting from $Me_2Si(OH)_2$ with the elimination of H_2O, a crude estimate comes up with $\Delta H^o = 0$, because we are just rearranging Si-O and O-H bonds in the process. Undoubtedly ΔH^o is negative for this latter process because of the significantly stronger Si-O bonds in alternating -Si-O-Si-O- polysiloxane chains (recall the stronger Si-O bond in $(Me_3Si)_2O$).

(iii) Polycarbosilane from polysilane



$$\left[-\overset{Me}{\underset{Me}{Si}}-\right]\overset{Me}{\underset{Me}{Si}}- \rightarrow \left[-\overset{Me}{\underset{H}{Si}}-CH_2-\right]\overset{Me}{\underset{H}{Si}}-CH_2-$$

$$\begin{aligned}\Delta H^o &= D(Si\text{-}Si) + D(C\text{-}H) - D(Si\text{-}C) - D(Si\text{-}H)\\ &= \quad 79 \quad + \quad 100 \quad - \quad 93 \quad - \quad 95\end{aligned}$$

$$\underline{\Delta H^o = -9 \text{ kcal mol}^{-1}}$$

The driving enthalpy here is rather small but again there is probably a strengthening of Si-C bonds in alternating -Si-C-Si-C- chains (just as for Si-O bonds in polysiloxanes) which would make the reaction more exothermic.

Because they are so important, I include additionally two more processes whose overall enthalpies are more easily related to *average* bond energies (although with some dissociation energies involved as well). The required values are shown in table 8 and are all estimated from known compounds, including solids!

(iv) The direct process

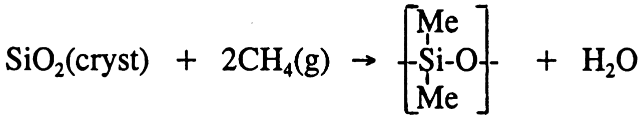
$$Si(cryst) + 2MeCl(g) \rightarrow Me_2SiCl_2(g)$$

$$\begin{aligned}\Delta H^o &= 2\bar{D}(Si\text{-}Si) + 2D(C\text{-}Cl) - 2\bar{D}(Si\text{-}C) - 2\bar{D}(Si\text{-}Cl)\\ &= 2 \times 54 \quad + \quad 2 \times 83 \quad - \quad 2 \times 86 \quad - \quad 2 \times 95\end{aligned}$$

$$\underline{\Delta H^o = -68 \text{ kcal mol}^{-1}}$$

This brings out clearly the strong driving forces of this reaction, *viz*, the significant gains in bond energy of Si-C over Si-Si and of Si-Cl over C-Cl.

(v) The dream process



$$SiO_2(\text{cryst}) + 2CH_4(g) \rightarrow \left[-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}-O-\right] + H_2O$$

$$\begin{aligned}\Delta H^\circ &= 2\bar{D}(\text{Si-O}) + 2D(\text{C-H}) - 2\bar{D}(\text{Si-C}) - 2\bar{D}(\text{O-H}) \\ &= 2 \times 111 + 2 \times 104 - 2 \times 76 - 2 \times 111\end{aligned}$$

$$\underline{\Delta H^\circ = +56 \text{ kcal mol}^{-1}}$$

This is clearly an endothermic process and could only be brought about with a significant energy input. The problem lies in the requirement to break the relatively strong C-H bonds compared to the Si-C bonds made. Interestingly the other requirement, *viz*, to break two (out of four) of the Si-O bonds, is compensated for by the strengths of the O-H bonds formed in the by-product water molecule. Although varients on this reaction have been reported with retention of all four Si-O bonds, the prospect of replacing two of them by Si-C bonds in any kind of direct reaction looks remote from the thermochemical viewpoint.

Summary

This brief review provides current values of key dissociation energies of the commonly encountered bonds in organosilicon compounds. They are used to illustrate, by rapid estimate, the thermochemical viability of several of the well-known commercial processes. It is hoped that the availability of these numbers, and this rapid estimate approach, will encourage organosilicon chemists in their search for new and viable organosilicon processes of the future.

Some general references

R. Walsh, "Bond dissociation energy values in silicon-containing compounds and some of their implications", *Accounts of Chemical Research*, **1981**, *14*, 246-252.

R. Walsh, "Thermochemistry", chapter 5 in *The Chemistry of Organic Silicon Compounds*, eds S.Patai and Z. Rappoport, John Wiley and Sons Ltd, **1989**, pp 371-391.

R. Becerra and R. Walsh, "Thermochemistry", Chapter 6 in *The Chemistry of Organosilicon Compounds*, eds Z. Rappoport and Y. Apeloig, John Wiley and Sons Ltd, **1998** in press.

S.W. Benson, *Thermochemical Kinetics*, John Wiley and Sons, 2nd edn, **1976**,

J. Berkowitz, C.B. Ellison and D. Gutman, "Three methods to measure RH bond energies", *Journal of Physical Chemistry*, **1994**, *98*, 2744-2765.

Table 1 Some Si-H bond dissociation energies (kcal mol^{-1})

Bond	*D*(Si-H)
H_3Si-H	91.8
Me_3Si-H	94.6
Ph_3Si-H	88.7
$(Me_3Si)_3Si$-H	84.7
Cl_3Si-H	94.4
F_3Si-H	103.3
H_3SiSiH_2-H	89.4
$PhSiH_2$-H	91.3

Table 2 Some Si-C bond dissociation energies (kcal mol^{-1})

Bond	*D*(Si-C)
H_3Si-Me	89.6
$MeSiH_2$-Me	91.1
Me_2SiH-Me	92.5
Me_3Si-Me	94.2
Me_3Si-Et	92.3

Table 3 Some Si-Si bond dissociation energies (kcal mol^{-1})

Bond	*D*(Si-Si)
H_3Si-SiH_3	76.7
H_3Si-Si_2H_5	74.8
H_5Si_2-Si_2H_5	73.1
Me_3Si-$SiMe_3$	79.3

Table 4 Some Si-halogen bond dissociation energies (kcal mol^{-1})

Bond	*D*(Si-X)	Bond	*D*(Si-X)	Bond	*D*(Si-X)
H_3Si-F	152	Me_3Si-F	158	F_3Si-F	167
H_3Si-Cl	109	Me_3Si-Cl	117	Cl_3Si-Cl	110
H_3Si-Br	90	Me_3Si-Br	102	Br_3Si-Br	90
H_3Si-I	71	Me_3Si-I	82	I_3Si-I	68

Table 5 Some Si-O and SiO-X bond dissociation energies (kcal mol^{-1})

Bond	*D*(Si-O)	Bond	*D*(SiO-X)
Me_3Si-OH	133	Me_3SiO-H	118
Me_3Si-OMe	123	Me_3SiO-Me	96
Me_3Si-OEt	122	Me_3SiO-Et	98
Me_3Si-$OSiMe_3$	136		

Table 6 Some Si-N and SiN-X bond dissociation energies (kcal mol^{-1})

Bond	*D*(Si-N)	Bond	*D*(SiN-X)
Me_3Si-NHMe	100	$(Me_3Si)_2N$-H	111
Me_3Si-NMe_2	98	$(Me_3Si)_2N$-Me	87
Me_3Si-$N(SiMe_3)_2$	109		

Table 7 Some π-bond energies (kcal mol^{-1})

Bond	$D_\pi(Si{=}X)$	Bond	$D_\pi(C{=}C)$
$H_2Si{=}CH_2$	37	$H_2C{=}CH_2$	65
$H_2Si{=}SiH_2$	27		
$H_2Si{=}O$	61	$H_2C{=}O$	75

Table 8 Some average bond energies (kcal mol^{-1})

Bond	$\bar{D}$(Si-X)
Si-Si	54
Si-C	76
Si-Cl	95
Si-O	111