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THE π-BOND ENERGY IN SILICO-OLEFINS

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SUMMARY

Recent kinetic and thermochemical data is analysed to set limits on the π bond energy, D_π, in methylenedimethylsilane of 119 kJ/mol $< D_\pi <$ 192 kJ/mol. A rather more approximate limit of $<$ 158 kJ/mol may be set for the π-bond energy in methylmethylenesilane. These figures indicate that the π-bond between Si and C is about half as strong as that in olefins.

INTRODUCTION

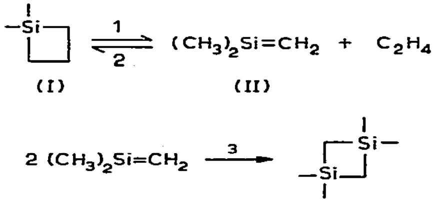
Contrary to early belief that second row elements do not participate in p_π–p_π bonding, there is rapidly accumulating evidence[1] of molecules containing such bonding. For example, methylenedimethylsilane[2], $(CH_3)_2Si{=}CH_2$ and dimethylsilanone[3], $(CH_3)_2Si{=}O$, have been shown by trapping experiments to be intermediates in the pyrolyses of 1,1-dimethylsilacyclobutane and octamethylcyclotetrasiloxane respectively. Rather than no π-bonds, these compounds contain weak but highly reactive π-bonds. The strength of the π-bond is an important index of reactivity[4] and a quantitative measure of it is therefore of value. Sufficient information now exists to set fairly restricted limits on the values for silico-olefins.

CALCULATION AND RESULTS

The desired values for the limits on D_π can be obtained from consideration of the kinetic data from two pyrolytic studies, *viz.* those of 1,1-dimethylsilacyclobutane by Flowers and Gusel'nikov[2] and trimethylsilane by Davidson and Lambert[5].

(*i*). *The pyrolysis of* 1,1-*dimethylsilacyclobutane*

Flowers and Gusel'nikov proposed the following mechanism:



for which they obtained the kinetic data:

$$\log k_1/\text{s}^{-1} = 15.64 \pm 0.30 - 262 \pm 3 \text{ kJ/mol}/2.303\, RT$$

and

$$\log k_2/k_3^{\frac{1}{2}}\, M^{-\frac{1}{2}}\, \text{s}^{-\frac{1}{2}} = 3.3 \pm 1.2 - 61 \pm 17 \text{ kJ/mol}/2.303\, RT$$

In the treatment that follows limits are set on the enthalpy change, $\Delta H^0_{1.2}$, which is, in turn, related to D_π. An upper limit for $\Delta H^0_{1.2}$ is readily obtained from the reasonable assumption that $E_3 > 0$, in which case, from the above data, $E_2 > 44$ kJ/mol and $\Delta H^0_{1.2}$ $(= E_1 - E_2) < 218$ kJ/mol. A lower limit for $\Delta H^0_{1.2}$ is more difficult to arrive at but can be obtained from the fact that methylenedimethylsilane (II) does not accumulate in the system. In other words reaction (3) is sufficiently fast to keep $[(CH_3)_2Si{=}CH_2]$ low. This gives a lower limit for k_3 and thence k_2. This latter is readily related to the lower limit for $\Delta H^0_{1.2}$.

A reasonable analytical detection limit of $[\text{II}] \leqslant 0.1\, [\text{I}]$ may be set for this study[*,†]. The stationary state treatment for (II) gives

$$k_1 \cdot [\text{I}] = k_2 \cdot [\text{II}] \cdot [C_2H_4] + 2k_3 \cdot [\text{II}]^2$$

At the outset of decomposition $[C_2H_4] = 0$ and $k_1 \cdot [\text{I}] = 2k_3 \cdot [\text{II}]^2$; thence from the limit above:

$$k_1 \cdot [\text{I}] < 0.02\, k_3 \cdot [\text{I}]^2$$

or

$$k_3 > 50\, k_1/[\text{I}]$$

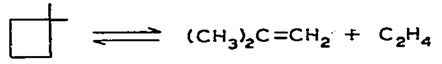
From the quoted experimental data for k_1 at typical conditions of these experiments (700 K and 10 mm):

$$k_3 > 18 \text{ M}^{-1} \cdot \text{s}^{-1}$$

And hence from the experimental ratio for $k_2/k_3^{\frac{1}{2}}$ at 700 K:

$$k_2 > 0.25 \text{ M}^{-1} \cdot \text{s}^{-1} \quad \text{and} \quad k_1/k_2 < 3.2 \times 10^{-4} \text{ M}$$

Thus $\Delta G^0_{1.2}$ $(= R \cdot T \cdot \ln(k_1/k_2)) > 46.8$ kJ/mol and $\Delta H^0_{1.2}$ $(= \Delta G^0_{1.2} + T \cdot \Delta S^0_{1.2}) > 46.8$ kJ/mol $+ T \cdot \Delta S^0_{1.2}$. The value of $\Delta S^0_{1.2}$ is not known but may be taken to be the same[**] as that for the analogous equilibrium:



for which group additivity[6] gives the value, at 700 K:

$$\Delta S^0_{1.2} = 144.5 \pm 4.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \text{ (1 mol/l standard state).}$$

Thus finally we have:

$$\Delta H^0_{1.2} > 46.8 \pm 98.4 = 145.2 \text{ kJ/mol}$$

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[*] The authors claim uncertainty of ±10% between overall pressure measurements and VPC analysis of product mixtures.

[**] Ref. 4, p. 38–41, discusses the principle of constant increments in S^0 for compounds of similar structure.

[†] *Note added in proof.* I. M. T. Davidson and J. M. Thompson (Private Communication) argue that a higher value for [II] is not ruled out.

The enthalpy change for $\Delta H^0_{1.2}$ is related to bond strengths as follows:

$$\Delta H^0_{1.2} = D(\mathrm{Si{=}C}) + D(\mathrm{C{-}C}) - D_\pi(\mathrm{Si{=}C}) - D_\pi(\mathrm{C{=}C}) = E \text{ (ring strain)}$$

All of these values are known except for the ring strain energy in (I). A value of 79 kJ/mol may be assumed for this by analogy* with the figure[6] for thietane (trimethylene sulphide).

Thus $\Delta H^0_{1.2} = 320$ (ref. 5) $+ 343$ (ref. 7) $- D_\pi(\mathrm{Si{=}C}) - 247 - 79 = 337 - D_\pi(\mathrm{Si{=}C})$. But since we have established that $145 < \Delta H^0_{1.2} < 218$, then $114 < D_\pi(\mathrm{Si{=}C}) < 119$.

(ii). The pyrolysis of trimethylsilane

Lambert and Davidson found a complex product mixture consisting of hydrogen, methane and several products containing two Si atoms including some disilacyclobutanes. From their kinetic measurements on H_2 and CH_4 formation they argue for a non-chain mechanism initiated by:

$$(CH_3)_3SiH \xrightarrow{4} CH_3^{\bullet} + (CH_3)_2\dot{S}iH$$

and

$$(CH_3)_3SiH \xrightarrow{5} H^{\bullet} + (CH_3)_3\dot{S}i$$

with CH_4 and H_2 formed via abstractions by $CH_3^{\bullet}$ and $H^{\bullet}$ respectively from $(CH_3)_3SiH$ and other products arising from radical-radical reactions amongst $(CH_3)_3Si^{\bullet}$, $CH_2^{\bullet}Si(CH_3)_2H$ and $(CH_3)_2\dot{S}iH$. The disilacyclobutanes come from dimerisations of $(CH_3)_2Si{=}CH_2$ and $CH_3SiH{=}CH_2$, argued to arise from disproportionation reactions. If this is so, then, even the most likely chain cycle**:

$$(CH_3)_2SiH\dot{C}H_2 \xrightarrow{6} (CH_3)SiH{=}CH_2 + CH_3^{\bullet}$$

$$CH_3^{\bullet} + (CH_3)_3SiH \xrightarrow{7} (CH_3)_2SiH\dot{C}H_2 + CH_4$$

is too slow to contribute to product formation. This sets an effective upper limit on the magnitude of k_6. The chain length of this hypothetical chain is approximately given by***:

$$\text{Chain length} = k_6/(k_4 \cdot k_8 \cdot [(CH_3)_3SiH])^{\frac{1}{2}}$$

where 8 is the radical termination process:

$$2\,(CH_3)_2SiH\dot{C}H_2 \xrightarrow{8} \text{Products}$$

The non-observation of the chain reaction implies that:

$$\text{chain length} < 1 \quad \text{or} \quad k_6 < (k_4 \cdot k_8[(CH_3)_3SiH])^{\frac{1}{2}}$$

From the quoted experimental data for k_4 at the typical conditions of these experiments

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* Heterocyclic rings of a given size are known to have similar strain energies for hetero atoms in the same row of the periodic table[6].

** The fastest chain cycle, by analogy with Rice Herzfeld chains, will involve methyl rather and H elimination steps. Step (6) is the only plausible such process.

*** This assumes that (8) is the principle termination process. Though other termination products in addition to those expected from (8) were observed, this introduces no serious error.

(1000 K, 10 mm) and an estimated value for k_8, assumed independent of temperature*:

$$k_6(1000\ \text{K}) < 10^{2.95}\ \text{s}^{-1}.$$

This unimolecular reaction will be close to its high pressure limit** under these conditions and by analogy with the similar alkyl decomposition may be expected[8] to have an A factor of $10^{13.0}\ \text{s}^{-1}$. This leads to $E_6 > 193$ kJ/mol, Methyl radicals are likely to add more readily to silico-olefins than to olefins which suggests an upper limit of $E_{-6} = 31$ kJ/mol[8]. Thus $\Delta H^{0}_{6,-6} > 162$ kJ/mol, but $\Delta H^{0}_{6,-6}$ is related to bond strengths as follows:

$$\Delta H^{0}_{6,6} = D(\text{Si–C}) - D_\pi = 320\ (\text{ref. } 5) - D_\pi$$

Hence $D_\pi < 158$ kJ/mol.

DISCUSSION

The calculations and estimates presented here rest on reasonable kinetic and thermochemical assumptions and the limits on D_π have been increased to take account of maximum errors in the experimental work analysed. The limits are therefore fairly conservative.

π-Bond energies among olefins are fairly insensitive to substitution[4] and the same is expected to apply amongst silico-olefins. Thus the values for methylenedimethylsilane and methylenemethylsilane should be similar. The figures presented here suggest $D_\pi \simeq 138 \pm 22$ kJ/mol. This is not far different from a much cruder estimate of 117 kJ/mol based on dissociation energy of Si=C[9].

Jackson[9] has pointed out that these weak π-bonds ($\approx \frac{1}{2}$ the values for olefins) imply not instability toward unimolecular decomposition but rather very reactive behaviour for silico-olefins in bimolecular reactions with other molecules. Preliminary figures, again rather crude, suggest that the π-bond in silico-ketones[3] is also $\approx \frac{1}{2}$ the value for ketones.

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* k_8 assumed equal to $10^{10.3}\ \text{M}^{-1}\cdot\text{s}^{-1}$ by analogy with other primary alkyl radical recombinations.

** A rough Kassel treatment gave $k/k_\infty = 0.84$.