

Derivation of thermodynamic quantities from kinetic measurements

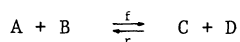
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Abstract - Results are presented of both traditional equilibrium and also gas phase kinetic measurements. These results are used to show, - (1) that measured enthalpies of formation of the fluorosilanes are probably in error, (2) a β -silicon substituted alkyl radical is stabilised by *ca* 12 kJ mol⁻¹ and (3) the simplest divalent silicon species, SiH₂, has an enthalpy of formation of 273 ± 6 kJ mol⁻¹, some 30 kJ mol⁻¹ higher than earlier estimates.

INTRODUCTION

Traditional methods of determining thermodynamic quantities centre on *calorimetry* and the study of *equilibria* (ref. 1,2). These methods are appropriate for pure stable compounds and clean reactions but are not generally possible for reactive species of lower (or higher) valence states than those commonly encountered. An approach which has proved useful for such species is that based on a variant of the equilibrium law, viz. the principle of microscopic reversibility (see e.g. ref. 3). In a reversible process such as



the equilibrium constant K is obtained as the ratio of forward and reverse state constants k_f/k_r . This procedure is valid provided the elementary processes can be clearly identified and their rate constants measured under identical conditions (with the proper maintenance of a Boltzmann distribution over internal states for all species). Measurements of rate constants can therefore be used to obtain useful thermodynamic information on a variety of interesting, reactive species.

In this article, I describe some selected results of the application of both conventional equilibrium and rate studies to the determination of thermodynamic quantities, particularly enthalpies of formation for a variety of silicon-containing molecules. Since a substantial part of our studies has already been published (ref. 4,5,6) the emphasis here is on recent findings and remaining uncertainties.

EQUILIBRIUM MEASUREMENTS

We have applied the equilibrium method to the determination of reliable ΔH_f^\ominus values for the methylsilanes (ref. 5). The advantage of this method is that even rough values for K can lead to quite precise values for ΔG^\ominus (an uncertainty of ±10% in K corresponds to ±0.24 kJ mol⁻¹ in ΔG^\ominus at 298 K; an uncertainty usually beyond the capability of calorimetry). If a reliable (third law) value of ΔS^\ominus is available this small uncertainty transfers to ΔH_f^\ominus . This approach was used to obtain the enthalpy changes for catalysed disproportionation equilibria involving methylsilanes. These results were then combined with known values for $\Delta H_f^\ominus(\text{SiH}_4)$ and $\Delta H_f^\ominus(\text{Me}_4\text{Si})$ to obtain ΔH_f^\ominus for the other (three) methylsilanes (ref.5).

Disproportionation enthalpies are themselves both interesting and revealing. Our data on the methylsilanes (Table 1) are compared with estimates for the chloro- and fluoro-silanes based on evaluated (ref. 6) or experimental values (ref. 7) for ΔH_f^\ominus . The relatively small ΔH^\ominus values for the methyl- and chloro-silane reactions indicate that X-for-H substitution

TABLE 1. Disproportionation enthalpies for substituted silanes in kJ mol⁻¹ (298 K)

Reaction	X ≡	Me ^a	Cl ^b	F ^c
2XSiH ₃ ⇌ SiH ₄ + X ₂ SiH ₂		-2.1	-9.6	+61.9
2X ₂ SiH ₂ ⇌ XSiH ₃ + X ₃ SiH		-3.2	-4.6	-33.5
2X ₃ SiH ⇌ X ₂ SiH ₂ + X ₄ Si		-1.1	+10.5	+32.6

^a ref. 4 ^b ref. 6 ^c ref. 7

produces an approximately constant effect. This is equivalent to constancy of bond enthalpy contributions (bond additivity). While the data for fluorosilanes might well be expected to show some deviations from bond additivity (i.e. non-negligible bond-interaction terms) the apparently large and alternating disproportionation values seem excessive and unreasonable (ref. 6). This suggests that there may be some errors in fluorosilane heats of formation (ref. 7). These could therefore usefully bear re-measurement.

KINETIC MEASUREMENTS

Two types of investigation have been carried out. One is concerned with the measurement of bond dissociation enthalpies using a kinetic iodination technique (ref. 4) and the other involves a method of measuring rates of silylene reactions (ref. 8), which, combined with pyrolytic information yields silylene heats of formation.

Gas phase iodination kinetics

The technique has been described in detail (ref. 4) and so only an outline is given here. The basis of the method involves study of the iodine abstraction process



E_1 the activation energy of step (1) is measured directly and E_2 (believed small) is estimated. The justification for estimation is based on the proposition that small errors in E_2 lead to only small errors in ΔH^\ddagger . Conditions of measurement are always such that the desired elementary process can be isolated and a thermal (Boltzmann) distribution of energy pertains. Once $\Delta H_{1,2}^\ddagger$ is known it can be used, after correction to 298 K either to obtain ΔH_f^\ddagger for the radical R' (provided ΔH_f^\ddagger (RH) is known) or the bond dissociation enthalpy, $D(R-H)$, via

$$D(R-H) = D(H-I) + \Delta H_{1,2}^\ddagger$$

Recently we have used this method to obtain quantitative information on certain interactions in silicon-substituted alkyl radicals. The radicals concerned are shown in Fig. 1.

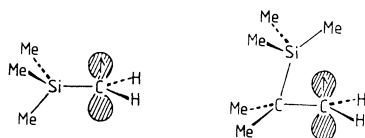


Fig. 1. α - and β - silicon substituted alkyl radicals, generated *via* I-atom abstraction.

TABLE 2. Some Bond Dissociation Enthalpies in kJ mol^{-1}

Bond	$D(R-H)$		Reference
	a	b	
$\text{Me}_3\text{CCH}_2\text{-H}$		417	11
$\text{Me}_3\text{SiCH}_2\text{-H}$	415 ± 5	415	11
$\text{Me}_3\text{SiCMe}_2\text{CH}_2\text{-H}$	410 ± 11	405	12

a Based on E_1 only.

b Based on a collision theory A factor estimate

There is plenty of evidence for the existence of α - and β - interactions (ref. 9,10) and their magnitudes may be assessed by comparison of C-H dissociation energies in the appropriate molecules with a suitable reference value. The measured data are shown in Table 2. To reduce scatter in the results the measured rate constants are fitted to an A factor estimated *via* collision theory which is known to fit other iodine atom abstraction processes quite well (based on data from studies cited in ref. 4). Such a procedure is the kinetic equivalent of the so-called "third law" method of obtained enthalpy changes from equilibrium constants in Thermodynamic experiments. Thus provided the neopentyl radical, Me_3CCH_2 , is accepted as a reference with no special interaction, then the α -silicon stabilisation (in Me_3SiCH_2) is *ca* 2 kJ mol^{-1} while the β -silicon stabilisation (in $\text{Me}_3\text{SiCMe}_2\text{CH}_2$) is *ca* 12 kJ mol^{-1} . Thus, as foreshadowed (ref. 4), β -stabilisation is the more substantial. The origin of this effect is discussed elsewhere (ref. 12). The magnitude of β -substituent effects for elements other than silicon is not known but clearly they are likely to be of great importance for organometallic free radical chemistry in general.

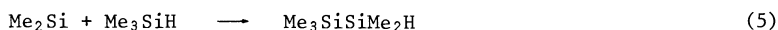
Gas phase silylene insertion kinetics

Silylenes, SiX_2 , are known to be substantially stabilised by an s^2 lone pair effect (ref. 4, 6). The establishment of stabilisation energies, and their influence by substituents (X) depends, in part, on a knowledge of $\Delta H_f^\ddagger(\text{SiX}_2)$. An important general source of such data are kinetic studies on the decomposition reactions



and their reverse reactions, the SiX_2 insertion processes. Many pyrolytic studies, of silicon compounds, particularly of disilanes, have been carried out by the groups of Purnell, Davidson and Ring & O'Neal. Some of these are cited in our own recent work (ref. 13) on Si_2F_6 pyrolysis. All these studies give values for E_3 , the activation energy for

decomposition of a particular silane (or disilane). If thermodynamic data, such as $\Delta H_f^\circ(\text{SiX}_2)$ are required, however, not only do the enthalpies of formation of the other species need to be known but also E_4 , the SiX_2 insertion barrier. Until recently experimental values for such barriers were unknown and could only be estimated approximately. In the past two years, however, a number of direct, time-resolved rate studies have appeared for SiCl_2 (ref. 14), SiF_2 (ref. 15) and SiH_2 (ref. 16,17) in the gas phase and SiMe_2 (ref. 18) and SiMePh (ref. 19) in solution. We have used the data for SiMe_2 to estimate a barrier for the insertion process



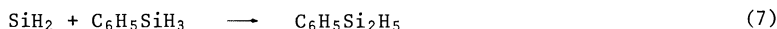
and thereby derived $\Delta H_f^\circ(\text{SiMe}_2)$ (*vide infra* and ref. 20). This ought to give an improved value over earlier estimates but it should be borne in mind that the direct study of SiMe_2 was carried out in solution (cyclopentane). A confirmatory gas phase study is highly desirable to rule out the possible complication of solvation effects.

The direct gas phase work on SiCl_2 and SiF_2 does not yet offer any example of a reaction which may be usefully exploited to obtain enthalpies of formation (which are anyway available from equilibrium studies (ref. 6)). However, the work on SiH_2 has provided both new data and a lively controversy. Using time-resolved laser absorption, Jasinski (ref. 17) obtained a rate constant (298 K) of $1.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction of SiH_2 with D_2 . The choice of D_2 rather than H_2 was to minimize reverse decomposition to SiH_2 of vibrationally-excited (unstabilised) SiH_2D_2 . Thus Jasinski was able to argue that his rate constant represented, to a close approximation, that for



Jasinski argued that his result supported an upward revision of $\Delta H_f^\circ(\text{SiH}_2)$ from an oft-quoted value of 243 kJ mol^{-1} (ref. 4) close to a figure of 285 kJ mol^{-1} obtained by theoretical calculation (ref. 21). The earlier figure for $\Delta H_f^\circ(\text{SiH}_2)$ was based on an estimate for k_6 which was $\approx 10^4$ lower than that recently measured.

We (ref. 22) have investigated this system using the photodecomposition of phenylsilane ($\lambda = 206 \text{ nm}$, $T = 100^\circ\text{C}$) as a source of SiH_2 and a competitive technique (ref. 8) in which rates of reaction of SiH_2 are measured relative to that for



Reaction (6) was studied over a pressure range and found, as expected, to be pressure dependent (i.e. not strictly second order). This is an indication of a non-Boltzmann distribution of energized SiH_4 molecules. By means of theoretical (RRKM) modelling we were able to establish that k_6^∞/k_7 was 0.017 (to within a factor of 2) where k_6^∞ represents the limiting (second order) rate constant (thermalized energy distribution). The absolute rate constant for k_7 was established *via* our relative rate studies (ref. 8) and direct measurements of Inoue and Suzuki (ref. 16). This led to k_6^∞ (373 K) = $1.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in satisfactory agreement with Jasinski's value at 298 K for a fast reaction with little or no activation energy.

Because of uncertainties in our value, and the lack of a measured activation energy (E_6) we adopted a third law approach to the calculation of $\Delta H_{6,-6}^\circ$ (298 K). The SiH_4 decomposition rate constant (k_{-6}) was calculated from the known Arrhenius equation (ref. 23) and combined with Jasinski's value for k_6 to give, $K_{6,-6} = 7.0 \times 10^{34} \text{ atm}^{-1}$ and $\Delta G_{6,-6}^\circ = -199 \text{ kJ mol}^{-1}$. From tabulated entropies we obtained $\Delta S_{6,-6}^\circ = -133 \text{ JK}^{-1} \text{ mol}^{-1}$ and thereby $\Delta H_{6,-6}^\circ = -238 \text{ kJ mol}^{-1}$. Taken in conjunction with $\Delta H_f^\circ(\text{SiH}_4)$ (ref. 24) this yields $\Delta H_f^\circ(\text{SiH}_2) = 273 \text{ kJ mol}^{-1}$ with an uncertainty estimated to be no more than $\pm 6 \text{ kJ mol}^{-1}$.

This value lies closer to recent theoretical calculations (ref. 21) than the older estimated figure and must be regarded as more reliable. It is essentially equivalent to Jasinski's estimate (ref. 17) and close to another experimental figure of $289 (\pm 12) \text{ kJ mol}^{-1}$ obtained by Shin and Beauchamp (ref. 25) by measurements of the gaseous proton affinity of SiH_2 .

The previous value of $\Delta H_f^\circ(\text{SiH}_2)$ was based on arguments (ref. 26) concerning the reaction



We have been able to show (ref. 22) that the revised value of 273 kJ mol^{-1} for $\Delta H_f^\circ(\text{SiH}_2)$ is consistent with the forward and reverse rate constants in an absolute (third law) sense at 585 K provided the new directly measured k_9 is used (ref. 16). The data can also be reconciled with higher temperature, shock tube measurements of Si_2H_6 pyrolysis (ref. 27) provided careful account is taken of unimolecular fall-off effects (non-Boltzmann internal energy distribution of internal states). There are still some apparent difficulties over the Arrhenius parameters for reaction (8), but there is no longer data for this system which

is in complete conflict with the new $\Delta H_f^\circ(\text{SiH}_2)$. The lesson is that provided careful measurements are made of both forward and reverse reactions, provided due account is taken of non-Boltzmann (unimolecular fall-off) effects, and provided ancillary ΔH_f° data is available, such kinetic systems yield useful data on ΔH_f° for reactive intermediates.

A summary of present thermodynamic data on divalent silicon (silylene) species is provided in Table 3.

TABLE 3. Thermodynamic data for silylenes

Species	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	DSSE
SiH ₂	273 ± 6	81 ± 9
SiMe ₂	92 ± 8	134 ± 12
SiF ₂	-590 ± 8	205 ± 42
SiCl ₂	-169 ± 3	159 ± 17
SiBr ₂	-46 ± 8	142 ± 50
SiI ₂	92 ± 8	134 ± 54



Fig. 2. Diagram showing bond polarisation in SiX_2 , leading to likely lone pair orbital contraction.

As well as heat of formation data this also shows the divalent state stabilisation energy (DSSE) operationally defined as the difference between first and second dissociation enthalpies in any SiX_4 species. This is obtained from existing data (ref. 4, 6, 20) and the new $\Delta H_f^\circ(\text{SiH}_2)$. The figures lend support to the idea (ref. 6) that DSSE depends on the electronegativity of the substituent since clearly there is a correlation. This may be understood in terms of a *deshielding* effect (Fig. 2). The more electronegative the substituent the more the bonding electrons are attracted further from the silicon nucleus, thus increasing the attraction of the nucleus for the (largely s-type) lone-pair electrons

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