Kinetics of the Gas-phase Reaction between Iodine and Trimethylsilane and the Bond Dissociation Energy $D(Me_3Si-H)^{\dagger}$

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Received 18th April, 1975

The title reaction has been investigated in the temperature range 519-618 K. The only products, formed in equal quantities, were trimethylsilyl iodide and hydrogen iodide, Rates were found to be surface sensitive below about 560 K, but not so in the range 567-618 K where the rate law

 $-\frac{d[I_2]}{dt} = \frac{k[I_2]^{\frac{1}{2}}[Me_3SiH]}{1 + k'[HI]/[I_2]}$

was obeyed over a wide range of iodine and Me₃SiH pressures. This expression is consistent with an iodine atom abstraction mechanism and for the step.

 $I' + Me_3SiH \rightarrow Me_3Si' + HI$

$$\log (k_1/dm^3 \text{ mol}^{-1} \text{ s}^{-1}) = 10.9 - 82.3 \text{ kJ mol}^{-1}/RT \ln 10$$

has been deduced. From this the bond dissociation energy $D(Me_3Si-H) = (376\pm11) \text{ kJ mol}^{-1}$ (90 kcal mol⁻¹) is obtained. The implications of this value for the pyrolyses of organosilanes are discussed.

Reliable free radical thermochemistry is crucial to an understanding of gas phase kinetics and mechanisms. Whereas for many organic species good thermochemistry is available and kinetics and mechanisms are reasonably well understood,^{1, 2} in the area of organosilicon chemistry this is not so. Organosilane pyrolyses appear to occur via free radical pathways in many cases ³ and a complete understanding of their mechanisms depends heavily on a knowledge of Si—H and Si—Si bond dissociation energies. We decided therefore to attempt a measurement of $D(Me_3Si-H)$.

The most recent value,⁴ prior to our work, for $D(Me_3Si-H)$ was 340 kJ mol⁻¹. That this figure might be somewhat low was suggested by Whittle⁵ in the light of the relative rates of methyl radical abstraction from SiH₄^{6, 7} and Me₃SiH.^{6, 8} Relative HT yields from hot tritium atom abstractions ⁹ also indicate a higher figure. A recent redetermination by Davidson and Howard ¹⁰ of $D(Me_3Si-SiMe_3)$ used in combination with the appropriate thermochemistry leads to $D(Me_3Si-H) = 364$ kJ mol⁻¹.

Detailed kinetic studies of the gas phase reactions of iodine with many organic molecules have been exploited by Benson and co-workers ¹¹ to provide reliable bond dissociation energies. We extend this technique into the organosilicon field here by study of the reaction of iodine with trimethylsilane.

EXPERIMENTAL

APPARATUS

The apparatus consisted of a static vacuum system, and quartz reaction vessel located in an electrically heated metal block furnace, designed to allow passage of a light beam through

† A preliminary report of this work has appeared R. Walsh and J. M. Wells, *Chem. Comm.*, 1973, 513.

the vessel. The vessel contents could be continuously monitored by a single beam spectrophotometer (Hilger-Watts) the optics of which were modified for the purpose. The vessel, of path length ~17 cm, was connected to the vacuum system via a three-way tap the third arm of which was attached to a pressure transducer (Bell and Howell type 4-327-0003) which was heated to ~100°C, along with that section of the line used for handling I₂ vapour. Conventional silicone greased taps had to be used in this part of the line but otherwise greaseless valves (Springham) were employed.

Temperatures were measured with one of several chromel alumel thermocouples located next to the vessel. The calibration of the thermocouples was checked against an N.P.L. standard platinum resistance thermometer. Reaction vessel temperatures were controlled by an AEI RT3R proportional controller and were uniform in both space and time to within $\pm 1^{\circ}$ C.

Both the unpacked quartz vessel of S/V = 0.91 cm⁻¹, and an alternative one packed with Pyrex tubes (which still allowed passage of a narrow light beam) of S/V = 3.55 cm⁻¹, were washed with a dilute solution of silicone oil DC 703 in CCl₄ prior to use, to attempt to render their surfaces inactive.¹² Dead spaces were ~0.6 % and were neglected.

MATERIALS

Trimethylsilane was prepared by the LiAlH₄ reduction of trimethylsilyl chloride in dibutyl ether under nitrogen. Slight deterioration of the purified gas occurred over long periods leading to formation of small quantities of higher molecular weight materials (not identified). Because of this it was always redistilled through a -78° C trap prior to a day's experiments. It was identified by its i.r. spectrum ¹³ and contained no gas chromatographically detectable impurities (after redistillation).

Trimethylsilyl chloride was a gift from Midland Silicones.

Trimethylsilyl iodide was prepared ¹⁴ by the reaction of aluminium iodide with hexamethyl disiloxane (Koch Light). After distillation the fraction boiling at 106-107°C was collected. The product proved still to have substantial contamination with hexamethyldisiloxane (which could either be unreacted starting material or a hydrolysis product). The iodide was identified by its n.m.r. spectrum ¹⁵ (single line absorption at 9.28 τ). Further purification was not attempted because of the ease of hydrolysis of the iodide. The impure iodide was adequate for identification purposes since the contaminant does not absorb in the u.v. (above 210 nm).

Iodine (Koch Light 99.998 % pure grade) was degassed before each experiment.

Hydrogen iodide gas was prepared by adding an HI solution (Fisons AnalaR) dropwise on to P_2O_5 . It was dried by passage through a $-78^{\circ}C$ trap and collected at $-196^{\circ}C$. It was stored at room temperature in a blackened bulb and degassed before use.

PROCEDURE

Prior to a kinetic run, iodine $(at - 20^{\circ}C)$ and trimethylsilane $(at - 196^{\circ}C)$ were thoroughly degassed. I₂ was evaporated into the reaction vessel at a known pressure and, in most experiments its absorbance at a wavelength of 484 nm was recorded. A run was initiated by the sharing of a known pressure of trimethylsilane into the vessel. A continuous trace of the absorbance variation with time was recorded during runs which varied (according to conditions) from minutes to several hours. The pressure transducer was used to record pressures at intervals during a run, but was not left continuously in contact with reacting mixtures because of small losses due to slow absorption of I₂ into the transducer. In some runs absorbance traces were obtained at other wavelengths in both the visible and u.v. regions. The 484 nm absorbance traces represent a direct record of iodine consumption as a function of time since in the reaction mixture only iodine absorbs at this wavelength. Calibrations of the spectrophotometer showed that Beer's law was obeyed by iodine at 484 nm up to 2.0 absorbance units.

After a run the products were usually frozen out of the vessel and removed; they were only retained in preliminary identification experiments. Some runs were fairly short and so a test was devised to ensure that mixing times (for I_2 with Me₃SiH) were still negligible.

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Because I_2 vapour is visible this was easily done by eye in an identical vessel (at about 50°C) outside the oven. Even at 1 atm of added air mixing times were less than 3 s. Lower pressures and higher temperatures reduce this time.

In runs designed to study the inhibition by HI, the procedure was identical apart from initial addition of HI to the reaction vessel, after the I_2 but before Me₃SiH.

PRODUCT IDENTIFICATION

Qualitative identification of the products as HI and Me₃SiI was achieved simply by evaporating them sequentially into the vessel after a run, and recording their u.v. spectra. The u.v. spectra were in accord with those of authentic samples (see fig. 1). A more quantitative identification was made by attempting to monitor the absorbance at several u.v. wavelengths both during and after a run at 546 K. The absorbances at these wavelengths were calibrated against those of HI and Me₃SiI. The former was a pure sample. The latter, because of contamination of the prepared sample, was the triply distilled recovered sample from several actual runs. Fig. 1 shows a comparison between the runs of the absorbances/ pressure of HI and Me₃SiI (in Torr, 1 Torr = 133.2 N m^{-2}) and the final absorbance (based on pressure of I_2 consumed) of a particular run. The matching is reasonable although not perfect. The time evolution of u.v. absorbance at 220, 230, 250, 270 and 490 nm shows that [HI] and [Me₃SiI] must be within 10 % both of each other and of the decrease in $[I_2]$.



FIG. 1.—Comparison of the u.v. spectrum of reaction products at 546 K with the sum of u.v. spectra of HI and Me₃Sil. O, reaction products; ---, HI spectrum; ---, Me₃Sil spectrum; ----, sum of spectra.

Several species were specifically ruled out from consideration. Since the reaction product was completely condensible (≤ 0.5 % of total products remain in the vessel), hydrogen and methane were absent at this level. Methyl iodide could not have exceeded a few percent of the products based on chromatographic analysis (4 m length 15 % ppG column at 60° C), and substantial amounts of other iodides (such as Me₂SiHCH₂I) could not have been present or a u.v. absorption peak at ~ 260 nm would have been observed. Gas chromatographic analysis of the -78° C condensible reaction product on the column showed the only substantial peaks to be due to Me₃SiH (unreacted) and Me₃SiI. Some minor peaks totalling a few percent in area were present. However, as the iodide is partially hydrolysed in the sampling system and co-elutes with $(CH_3)_3$ SiOSi $(CH_3)_3$ the chromatographic analysis is not particularly reliable.

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RESULTS

PRELIMINARY EXPERIMENTS

The quantitative identification of the products points to the chemical process

$(CH_3)_3SiH + I_2 \rightarrow (CH_3)_3SiI + HI.$

This is supported by pressure measurements which indicate no pressure change (to within ± 0.3 Torr or better) during reaction. No secondary reaction between trimethylsilane and HI occurs as evidenced by a complete lack of any absorbance changes (in both visible and u.v.) when they were mixed at typical pressures at 547 K. Trimethylsilyl iodide was thermally stable under the conditions of our experiments.

Table 1 shows an example of some iodine decay data in an early run at 546 K, using 7.02 Torr I_2 and 21.3 Torr Me₃SiH.

TABLE 1.—IODINE DECAY WITH TIME								
time/min	0	4	8	12	16	20	24	28
I ₂ /Torr	7.02	6.26	5.73	5.24	4.74	4.37	4.01	3.71
time/min	32	36	40	44	48	52	56	60
I ₂ /Torr	3.37	3.06	2.75	2.46	2.14	1.87	1.65	1.42

These data were tested to find the order with respect to iodine, by the van't Hoff method. It was assumed that the reaction was first order in Me₃SiH, although since Me₃SiH was in excess this assumption was not very critical. A plot was made of $\log\{(\Delta I_2)/[Me_3SiH]_r\}$ against $\log[I_2]_r$ where ΔI_2 is the loss in I_2 over an 8 min interval (i.e., is an approximation to the rate) and [Me₃SiH], and [I₂]_r were the instantaneous concentrations at the middle of the interval, [Me₃SiH], being determined from stoichiometry and the I_2 decrease. This plot is shown in fig. 2. Such plots employing differences are always scattered but a forced straight line fit gives a slope (i.e., an order) of 0.47 ± 0.16 . A further test of this data was made by attempting to fit it to the integrated form of the rate equation on the assumption of half and first order dependence of the rate on I_2 and Me₃SiH respectively. The appropriate equation (see appendix) predicts a linear fit of $\tan^{-1}(f^{\frac{1}{2}})$ with time where $f = [I_2]_t/([Me_3SiH]_0 - [I_2]_0)$. Fig. 3 shows the plot for the data of table 1. The fit is reasonable although slight departures from linearity at long times were observed in many runs.

DETAILED KINETIC MEASUREMENTS

Further tests to establish the rate law consisted in measuring the three halves order rate constant, k_{a} , defined by

$$-d[I_2]/dt = k_*[I_2]^{\frac{1}{2}}[Me_3SiH]$$
(A)

by means of integrated plots and then examining the dependence of $k_{\frac{3}{2}}$ on starting conditions (particularly the ratio [Me₃SiH]/[I₂]). Most of the integrated plots showed slight curvature, indicating inhibition of the reaction at high conversions. This was subsequently allowed for explicitly but to avoid complications in these tests the decay plots were not examined beyond 50 % conversion of I₂. Good linear fits to the $\tan^{-1}(f^{\frac{1}{2}})$ against time plots were usually obtained up to this point. Table 2 shows some rate constants obtained at about 595 K.

Apart from one run the $k_{\frac{3}{4}}$ values scatter to a maximum of ± 15 % around the mean, and cover a range of values of the ratio [Me₃SiH]/[I₂] from 5-50. At all temperatures runs with this ratio less than two tended to give high values for $k_{\frac{3}{4}}$. Between values

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FIG. 2.—Log-log plot of rate against concentration to determine reaction order with respect to iodine at 546 K. Error bars represent uncertainty limits from spectrophotometric trace.



FIG. 3.—Plot of the rate data at 546 K according to the integrated rate equation. See text for definition of f.

[I ₂]/Torr	Me ₃ SiH/Torr	104k3/Torr-\$ s-1
2.03	64.6	3.59
4.95	45.3	4.11
1.30	22.3	3.49
1.55	7.7	3.21
4.66	22.5	4.19
8.28	10.5	5.73
2.29	117.1	3.58

TABLE 2.---A SELECTION OF RATE DATA AT 595 K

of 3 and 200, $k_{\frac{1}{2}}$ was constant within the scatter. This moderately high scatter could be attributed to instability and noise in the single beam spectrophotometric system. At the lower two temperatures the scatter became greater but this was shown to arise from surface effects. Within these limitations the rate data supported the three halves order expression (A) reasonably well.

Several runs were performed in the packed vessel to test for heterogeneity. Table 3 shows a selection of the results. It is clear from these data that substantial surface catalysis is occurring at 522 and 533 K. To try to reduce this effect both vessels were rewashed with silicone oil solution and the unpacked vessel with hexamethyldisilazane also. These treatments had little or no effect. At 581 K and higher temperatures the surface effect seemed to have disappeared and it probably was not serious in the unpacked vessel above 500 K.

TABLE 3.—COMPARISON OF RATE	CONSTANTS '	^a OBTAINED	IN DIFFERENT	VESSELS,	WITH	VARIOUS
	SURFACE	TREATMENT	S			

	temperature/K			
vessel, treatment	522	533	581	
unpacked, untreated	0.65	1.03	16.09	
unpacked, silicone oil washed	0.66	1.14	15.89	
unpacked, HMDS ^b washed	0.78	1.24	14.30	
packed, untreated	4.86	5.32	22.51	
packed, silicone oil washed	3.52	4.24	16.94	

^a $10^{5}k_{\frac{3}{2}}/\text{Torr}^{-\frac{1}{2}}\text{s}^{-1}$, ^b hexamethyldisilazane.

All rate constants were corrected for inhibition which raised their values by about 10 %. They were then put into an Arrhenius plot which is shown in fig. 4. The line shown is a least squares fit to all the data (over 100 runs in the temperature range 519-618 K) apart from runs in the packed vessel and runs with low values for the ratio $[Me_3SiH]/[I_2]$. This yields

Since at lower temperatures surface contributions in the unpacked vessel occurred, an alternative calculation was done for the limited temperature range 567-618 K yielding

$$\log(k_{*}/\text{Torr}^{-\frac{1}{2}} \text{ s}^{-1}) = (12.50 \pm 0.30) - (181.6 \pm 3.4 \text{ kJ mol}^{-1})/RT \ln 10.$$

The error limits quoted are one standard deviation (68 % confidence level).

To examine the inhibition phenomenon in more detail a series of runs was performed in which HI was added initially to the reaction mixtures. This was to enhance the effect and to try to minimise the errors associated with the analysis. Traces of iodine decay with time were obtained as before but these were now tested for consistency with the expression

$$-\frac{d[I_2]}{dt} = \frac{k_{\frac{1}{2}}[I_2]^{\frac{1}{2}}[Me_3SiH]}{1+k'[HI]/[I_2]}$$
(B)

shown later (see mechanism section) to fit the proposed mechanism. Rearrangement of eqn (B) gives

$$\frac{[I_2]^{\frac{1}{2}}[Me_3SiH]}{-d[I_2]/dt} = \frac{1}{k_{\frac{3}{2}}} + \frac{k'}{k_{\frac{3}{2}}} \frac{[HI]}{[I_2]}$$

Fig. 5 shows a test of this equation in which $-d[I_2]/dt$ is approximated by the change,

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FIG. 5.—Plot showing a test of the inhibition effect of HI on the reaction at 568 K.

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 $-\Delta I_2$, over a fixed but small time interval (4 min). To use such plots to obtain the values of k' (= slope/intercept), the intercepts were fixed by taking an average value of k_3 appropriate to the temperature in question. The data fit linear plots within the scatter where the error bars on each point represent maximum errors arising from uncertainties in the experimental traces. Fig. 6 shows an Arrhenius plot of the derived values of k' from such experiments. The temperature range here was limited to



FIG. 6.—Arrhenius plot for k'. See text for explanation of the two lines.

567-618 K to avoid any risks of surface contributions. The scatter is again large and the highest temperature point appears somewhat out of line with the others. Since these values depend somewhat on $k_{\frac{3}{2}}$ used in deriving them it is interesting to note that a lower $k_{\frac{3}{2}}$ value (which would bring it closer to its Arrhenius line) would reduce k' at this temperature and bring it closer to the line suggested by the other points. The two lines drawn correspond to inclusion and exclusion of this point. The corresponding Arrhenius lines are, respectively,

$$\log k' = (1.28 \pm 0.56) - (22.3 \pm 6.3 \text{ kJ mol}^{-1})/RT \ln 10$$

and

$$\log k' = (-0.19 \pm 0.59) - (6.1 \pm 6.5 \text{ kJ mol}^{-1})/RT \ln 10.$$

REACTION MECHANISM AND THE BOND DISSOCIATION ENERGY

The observed kinetics parallel very closely those between I_2 and hydrocarbons ¹⁰ and so, by analogy, the iodine atom abstraction chain mechanism below seems most likely;

$$I_{2}(+M) \rightleftharpoons 2I \cdot (+M)$$

$$I \cdot + Me_{3}SiH \rightleftharpoons^{1}_{2} Me_{3}Si \cdot + HI$$

$$Me_{3}Si \cdot + I_{2} \xrightarrow{3} Me_{3}SiI + I \cdot.$$

A stationary state treatment of this mechanism leads to

$$-\frac{d[I_2]}{dt} = \frac{k_1 K_{I_2}^{\dagger} [I_2]^{\dagger} [Me_3 SiH]}{1 + k_2 [HI]/k_3 [I_2]}.$$

$D(Me_3Si-H)$ bond dissociation energy

Thus by comparison with the experimental results both the order dependence and inhibition effect are accounted for. In addition k_3 can be identified with $k_1 K_{12}^{\frac{1}{2}}$ and k' with k_2/k_3 . From the known values ¹⁶ of K_{12} the following expressions for k_1 are obtained from either all the data, or only the higher temperature selection, respectively,

$$log(k_1/dm^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.90 - 71.2 \text{ kJ mol}^{-1}/RT \ln 10$$

13.35 - 110.2 kJ mol}^{-1}/RT ln 10.

or

These figures are unfortunately rather far apart and furthermore the more limited (second) set of parameters, apparently free from surface effects, gives an A factor rather higher than the collision number ($\sim 10^{11.3}$ dm³ mol⁻¹ s⁻¹). The total set of data probably gives an A factor which is too low because of the inclusion of surface effects. In the light of this, probably the best procedure is to select $A = 10^{10.9}$ dm³ mol⁻¹ s⁻¹ by analogy with the hydrocarbon case,^{11, 17} viz., I·+i-C₄H₁₀ \rightarrow Bu^t·+HI. By compensation of parameters this leads to

 $\log(k_1/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 10.90 - 82.3 \text{ kJ mol^{-1}}/RT \ln 10.$

The Arrhenius line corresponding to these parameters is very similar to one obtained by omitting the rate constants at the single highest and the two lowest temperatures. However, there is no compelling experimental reason for making such a selection.

Again comparison with hydrocarbon systems ¹¹ suggests that of the two possibilities for the inhibition constant the one where the highest temperature data are omitted is more likely. Hence

$$\log(k_2/k_3) = -0.19 - 6.1 \text{ kJ mol}^{-1}/RT \ln 10.$$

It seems reasonable to suppose that $E_3 = 0$ since alkyl radicals react with I₂ with no activation energy and Si—I bonds are probably stronger (see discussion) than C—I bonds.³ Hence $E_2 = 6.1$ kJ mol⁻¹. Thus, $\Delta H_{1,2}(593 \text{ K}) = E_1 - E_2 = 76.2$ kJ mol⁻¹. Correction of this enthalpy change to room temperature using $\Delta \bar{C}_p^\circ = -8.8$ J mol⁻¹ K⁻¹, estimated by thermochemical methods, ¹ yields $\Delta H_{1,2}^\circ$ (298 K) = 78.8 kJ mol⁻¹. Since $\Delta H_{1,2}^\circ = D(\text{Me}_3\text{Si}-\text{H}) - D(\text{H}-\text{I})$, then from the known value¹¹ of D(H-I) = 298 kJ mol⁻¹

$$D(Me_3Si-H) = 376 \text{ kJ mol}^{-1}$$
.

Error limits have not been included in the above figures because of the assumption about the A factor, which lay well outside the apparent precision of the data. It would seem most reasonable to assume that the A factor is within a factor of 10 of the true value in which case the uncertainty in $D(\text{Me}_3\text{Si}-\text{H})$ is $\pm 11 \text{ kJ mol}^{-1}$.

DISCUSSION

Despite the uncertainties in the data, the kinetics found for this reaction offer strong support for the atomic chain mechanism proposed. The only difference between this reaction and its hydrocarbon counterpart is the lack of reversibility of the overall process undoubtedly due to the more favourably negative enthalpy change which in turn arises from the increased strength of the Si—I bond relative to C—I.

A possible alternative atomic mechanism is worth considering;

$$I_{2}(+M) \rightleftharpoons 2I \cdot (+M)$$

$$I$$

$$I \cdot + Me_{3}SiH \rightarrow (Me_{3}Si) \rightarrow Me_{3}SiI + H \cdot$$

$$H$$

$$H \cdot + I_{2} \rightarrow HI + I \cdot.$$

The key step in this sequence is the displacement step (via a penta co-ordinated intermediate or transition state). However, it seems much more likely that if a displacement were to occur, methyl radicals rather than hydrogen atoms would be the product. No methyl iodide was detected amongst the products and so this mechanism appears unlikely.

Bond dissociation energies determined by this method ¹¹ are usually amongst the most reliable and so it is unfortunate that the error associated with the present determination is so large. Nevertheless our value of 376 kJ mol⁻¹ is in reasonable agreement with a figure of 364 kJ mol⁻¹ which may be derived from the latest determination of $D(Me_3Si-SiMe_3)^{10}$ and the appropriate heats of formation.²⁰ Davidson and Howard ¹⁰ also quote separate unpublished electron impact measurements leading to a value of 368 kJ mol⁻¹. Clearly the earlier figure ⁴ of 340 kJ mol⁻¹, obtained from data on the pyrolysis of Me₁SiH is too low. Our figure substantially reduces the discrepancy in relative methyl radical abstraction rates from SiH₄^{6,7} and Me₃SiH.^{6,8} On a per Si-H bond basis the rates are closely comparable, and the activation energies are extremely close, being 29 and 33 kJ mol⁻¹ respectively. The bond strengths for the two Si—H bonds, with $D(SiH_3-H) = 397\pm 5 \text{ kJ mol}^{-1},^{18}$ differ by 57 kJ mol⁻¹ on the basis of the old value ⁴ for $D(Me_3Si-H)$ but by only 21 kJ mol⁻¹ from the present figure. Unfortunately it is not possible to predict methyl radical abstraction rates from bond dissociation energies or the converse, but they are usually correlated.^{5, 19} It is still slightly surprising that, on a per bond basis, methyl radicals react faster with SiH4 with its stronger Si-H bond than with Me3SiH. Perhaps D(SiH₃-H), determined by electron impact studies,¹⁸ is slightly too high.

The correlation of HT yields from recoil tritium abstraction reactions has led Hosaka and Rowland ⁹ to suggest that $D(Me_3Si-H)$ is around 356 kJ mol⁻¹. However, the correlation line is curved and the present value is not incompatible with the curve. Yields of HT from Me_2SiH_2 and $MeSiH_3$ imply that $D(Me_2SiH-H)$ and $D(MeSiH_2-H)$ are about 2-3 kJ mol⁻¹ greater than $D(Me_3Si-H)$. We intend to investigate this point later.

Heat of formation data for silicon containing compounds have been somewhat unreliable in the past. A recent compilation ²⁰ gives $\Delta H_f^{\circ}(Me_3SiH) = -156 \text{ kJ mol}^{-1}$ which, taken in conjunction with our value for $D(Me_3Si-H)$, leads to $\Delta H_f^{\circ}(Me_3Si) =$ +2 kJ mol⁻¹. This figure is only on the borderline of compatibility with the value of -11 kJ mol⁻¹ derived by Davidson in the Me₃SiSiMe₃ pyrolysis work using $\Delta H_{\rm f}^{\circ}({\rm Me_3SiSiMe_3}) = -359 \, \rm kJ \, mol^{-1}.^{20}$ This suggests a possible remaining inconsistency between $\Delta H_{f}^{\circ}(Me_{3}SiH)$ and $\Delta H_{f}^{\circ}(Me_{3}SiSiMe_{3})$. Used in conjunction with other molecular heats of formation ²⁰ our value for $\Delta H_{\rm f}^{\circ}({\rm Me}_{3}{\rm Si})$ leads to higher figures for several bond dissociation energies. Noteworthy amongst these is the value of 380 kJ mol⁻¹ for $D(Me_3Si-Me)$. Although there is undoubtedly still some error associated with it, this value is quite a bit higher than that for the analogous carbon-carbon bonds. Apart from being surprising in itself, this fact, if true for other Si-C bonds, means that the initiation step in free radical organosilane pyrolyses will be considerably slower than was thought.^{4, 21} This in turn implies that chain sequences of the Rice-Herzfeld type, previously ruled out,⁴ are likely to occur. For example, in Me₃SiH pyrolysis

$$CH_3^{\bullet} + Me_3SiH \rightarrow CH_4 + \bullet CH_2SiHMe_2$$

$$\cdot CH_2SiHMe_2 \rightarrow CH_2 = SiHMe + CH_3$$

is a probable cycle. Because some products are common to both propagation and termination, the determination of chain lengths in these pyrolyses is not straightforward. The participation of divalent silicon intermediates 10.22 is a possible added complica-

tion and it is clear that these pyrolyses will need careful reinvestigation if their mechanisms are to be understood.

Another important thermochemical quantity, the π -energy in silico-olefins, was evaluated ²³ from earlier kinetic studies with organosilanes, as lying between 119 and 158 kJ mol⁻¹. In the light of the new Si—C bond dissociation energies this requires upward revision. A value close to 200 (\pm 20) kJ mol⁻¹ may be estimated using similar thermochemical arguments.²³ This new value means that these π -bonds have about 80 % of the strength of the π -bonds in olefins, considerably more than had been thought.^{23, 24} *

APPENDIX

Integration of the approximate rate equation (A) gives

$$an^{-1}(f^{\frac{1}{2}}) - tan^{-1}(f^{\frac{1}{2}}) = \frac{1}{2}(b-a)^{\frac{1}{2}}k_{\pm}t$$
 (C)

where $f = [I_2]/(b-a)$, $a = [I_2]_0$ and $b = [Me_3SiH]_0$.

The integrated form of eqn (B) containing both unknown constants k_3 and k', gave very imprecise values for them when fitted to the data. The method, described in the results section, of enhancing inhibition by HI addition to reaction mixtures gives inherently more precise values for k'. The implication of inhibition by HI is that the plots of eqn (C) should be slightly curved. However, although slight curvature is observed, allowance for curvature is best made by correcting the k_3 from the linear fit by an *average* inhibition term (~5-10 %). The data are insufficiently precise to warrant any more sophisticated treatment.

The authors acknowledge the provision of both an equipment grant and a maintenance grant (to J. M. W.) from the S.R.C. We thank Mrs. Diane King for help with some of the preparative work.

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