= 0.60 + 0.05 = 0.65, with ϕ_{10} evaluated at 0.03. Similarly at 123.6 nm, ϕ_H = 0.65 + 0.06 = 0.71 leading to a value of 0.12 for ϕ_9.

Summary and Conclusion

The vacuum-ultraviolet photolysis of vinylcyclopropane may be described in terms of seven primary reaction channels. These are given in Table VI.

The data used to arrive at Table VI, in part presented in Tables I–V, were collected with an estimated accuracy of better than 10% for the quantum yields. Larger error limits apply for radical yield determinations since the resulting quantum yields were obtained as a difference between two quantum values with their own error limits. Hydrogen yields required experimental conditions, and operation that also would be expected to produce increased error limits. In these cases, the estimated error is around 15%. This estimated error must also be extended to the reaction channels presented in Table VI.

It must be noted that insufficient data were collected at 106.7–104.8 nm to reliably evaluate the quantum yields of the primary reaction channels.

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Kinetics of the Gas-Phase Reaction between Iodine and Trimethylgermane and the Bond Dissociation Energy $D(Me_3Ge–H)$[1]

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The title reaction has been investigated in the temperature range 420–474 K. The only products, formed in equal quantities, were trimethylgermyl iodide and hydrogen iodide. Despite some surface sensitivity, the reaction was found to obey the nonsurface-dependent rate law $-d[I_2]/dt = k[I_2]^{1/2}[Me_3GeH]/(1 + k'[HI]/[I_2])$ provided that the ratio $[Me_3GeH]_0/[I_2]_0$ was sufficiently large. This expression is consistent with an iodine atom abstraction mechanism and for the step $I\cdot + Me_3GeH \rightarrow Me_3Ge\cdot + HI$ (1), $\log (k_1/dm^3\ mol^{-1}\ s^{-1}) = (9.94 \pm 0.10) - (45.3 \pm 0.9\ kJ\ mol^{-1})/RT \ln 10$, has been obtained. From this the bond dissociation energy $D(Me_3Ge–H)$ = 340 ± 10 kJ mol^{-1} (81 kcal mol^{-1}) is deduced. This value is compared with other estimates.

Introduction

Reliable free-radical thermochemistry is crucial to an understanding of gas phase kinetics and mechanisms. Such data for many organic free radicals are available and kinetics and mechanisms are reasonably well understood.[2] We have recently begun a program of study designed to provide information for organosilicon radicals via determination of bond dissociation energies in selected compounds viz. $D(X_3Si–H)$, where X = Me,[3] Cl,[4] and F[5] and $D(Me_3SiCH_2–H)$.[6] The method used has been the kinetic iodination technique developed by Benson and coworkers.[7] Very little information exists regarding bond strengths in organogermanium compounds and we extend the technique here to the determination of $D(Me_3Ge–H)$, its first application to a germanium containing compound.

There is no previous determination of $D(Me_3Ge–H)$ although there has been speculation as to its magnitude.[8] Most recently Austin and Lampe[9] suggested a value of 264 kJ mol^{-1} based on the semiempirical BEBO method for correlation of activation energies (H abstraction by H atoms) with dissociation energies. This method[10] is generally quite good for obtaining activation energies, E_a, from dissociation energies, D, but not usually the other way round because of the sensitivity of D to the precise value of E_a (and other parameters). Thus the estimated value is almost certainly too low and a better a priori estimate may be made from the value of $D(H_3Ge–H)$ and the assumption that Ge–H bond dissociation energies are probably not particularly sensitive to methyl substitution as seems to be the case for silanes.[11] $D(H_3Ge–H)$ is in the region of 326 kJ mol^{-1},[12] and by this argument so therefore should be $D(Me_3Ge–H)$.

Experimental Section

The previously described apparatus[3] has been improved by the incorporation of a new double beam spectrophotometer (Varian Techtron 635) in which the optics have been modified to allow one beam to make a double pass

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through the reaction vessel. This has led to an improvement in both sensitivity and stability.[3-5] For instance, I_2 pressures of as little as 0.2 torr (ϵ 359 dm^3 mol^{-1} cm^{-1} at λ 495 nm) could be monitored quantitatively with a precision of ±2%.

Trimethylgermane was prepared by a three stage synthesis starting from $GeCl_4$ (Johnson Matthey). The $GeCl_4$ was converted to $GeMe_4$ by means of a Grignard reaction.[13] After purification, $GeMe_4$ (95%) was converted to Me_3GeBr by bromination in the presence of isopropyl bromide.[14] After separation the Me_3GeBr was converted to Me_3GeH by $LiAlH_4$ reduction.[15] These are all standard procedures and are not therefore described in detail here. The Me_3GeH thus prepared was identified by IR[16] and mass spectrometry and was found to contain a small (ca. 10%) Me_3SiH impurity which could not be removed despite repeated distillations. Me_3SiH is a nonreactive impurity under the conditions of the work carried out here and so this impurity level was not felt to be a serious problem. However, a small quantity of another purer sample (>95%) of Me_3GeH was made from commercial Me_3GeBr and found to give identical results in several repeat experiments.

Iodine was obtained from Koch Light and hydrogen iodide gas was prepared by dehydration (P_2O_5) from solution (Fisons). The reaction products were identified as HI and Me_3GeI by mass spectrometry and IR,[17] after freezing down and separation by low pressure distillation. Small quantities of MeI were also detected (mass spectrum, gas-liquid chromatography). These, however, tended to accumulate during the time between the end of reaction and analysis. A limit could be set for MeI formed during reaction of ≤5% of the Me_3GeI and it was probably even less than this. A zero pressure change during reaction supplied further corroborative evidence that, on the time scale of these experiments, the only process occurring was

$$I_2 + Me_3GeH \rightarrow Me_3GeI + HI$$

Kinetic experiments were carried out as described previously[2] using a spectrophotometric method to monitor the iodine disappearance. Reaction times were from 1 min to 1 h. The majority of runs was performed in an unpacked reaction vessel (S/V = 0.72 cm^{-1}) but some runs were carried out in other vessels (S/V = 2.0 and 8.9 cm^{-1}).

Results

In accordance with general findings in gas phase iodination systems[3-7] a three-halves-order rate expression was adopted as a working hypothesis. The rate constant $k_{3/2}$ was defined by

$$-d[I_2]/dt = k_{3/2}[I_2]^{1/2}[Me_3GeH]$$

This expression was tested in two ways. First plots were made of the integrated form of the rate equation

$$\tan^{-1}(f^{1/2}) - \tan^{-1}(f_0^{1/2}) = -\tfrac{1}{2}(b - a)^{1/2}k_{3/2}t$$

where $f = [I_2]_t/(b - a)$, $a = [I_2]_0$, and $b = [Me_3GeH]_0$. ($[I_2]_t$ being the instantaneously measured iodine pressure at time t.) Good linear plots of $\tan^{-1}(f^{1/2})$ against t were obtained up to 50% conversion and usually as far as 75% conversion although slight upward curvatures were evident at higher conversions. This curvature arises from inhibition and in this test it was neglected (leading to a systematic 5% underestimate of $k_{3/2}$ obtained from the slope of these plots up to 50% conversion).

In the second test the possible dependence of $k_{3/2}$ upon starting pressures of reactants was investigated. Table I shows a set of results obtained at 463 K. It is clear from these data that $k_{3/2}$ is not precisely constant but varies by about 20% with conditions. The variation correlates with the ratio $[Me_3GeH]_0/[I_2]_0$ and Figure 1 shows this variation. It is apparent that the $k_{3/2}$ values are constant within reasonable experimental error when the ratio is greater than ca. 20 but that below this value $k_{3/2}$ tends to rise.

TABLE I: Rate Data for I_2 + Me_3GeH at 463 K

$[I_2]_0$/torr	$[Me_3GeH]_0$/torr	$10^5k_{3/2}$/ torr$^{-1/2}$ s^{-1}
6.57	7.6	10.4
3.31	13.5	9.41
3.45	24.2	8.92
3.28	27.6	8.81
3.25	29.7	8.11
2.92	37.1	8.47
3.27	56.4	8.49
1.53	37.3	8.29
1.61	51.2	8.14
1.45	47.8	8.22
1.56	65.4	8.20
0.31	19.3	8.01

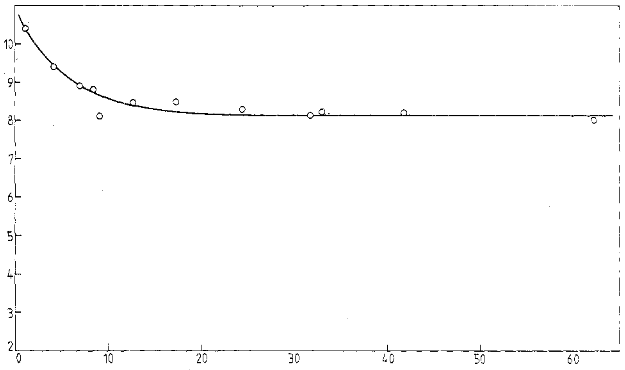


Figure 1. Variation of the rate constant $k_{3/2}$ with initial reactant ratio: (ordinate) $10^5 \times k_{3/2}$/torr$^{-1/2}$ s^{-1}; (abscissa) $[Me_3GeH]_0/[I_2]_0$.

This observation suggested that there may be an additional term in the rate equation when $[Me_3GeH]_0/[I_2]_0 < 20$. Such a term would have to be either of order greater than a half in I_2 or of order less than one in Me_3GeH (or both). There is some support for an extra term of the form $k_a[I_2][Me_3GeH]^{1/2}$ from the fact that a plot of $k_{3/2}$ against $\{[I_2]_0/[Me_3GeH]_0\}^{1/2}$ is linear. Unfortunately while this is true at this temperature, the fit is much poorer at other (particularly lower) temperatures. For this reason and because the reaction was very surface sensitive (vide infra) we abandoned attempts to find a universal rate equation appropriate to all conditions. Instead, the dependence of $k_{3/2}$ values on the reactant ratio was examined empirically at each of ten different temperatures in the range 420–474 K. Except at 420 and 426 K, limiting values of $k_{3/2}$ were always obtained although at the lower temperatures (431 and 437 K) the ratio $[Me_3GeH]_0/[I_2]_0$ required was as high as ca. 100.

In an investigation of the surface sensitivity, reaction rates in the packed vessel of highest surface-to-volume ratio (S/V = 8.9 cm^{-1}) were found to be very much higher than those in the unpacked vessel under similar reactant pressures (factors of ca. 10) even at the highest temperature. Thus a second series of tests was carried out in a vessel of intermediate surface-to-volume ratio (S/V = 2.0 cm^{-1}). After a conditioning period of several runs, rate constants $k_{3/2}$ were found to be in good agreement with unpacked vessel values at 474 K ($[Me_3GeH]_0/[I_2]_0 > 10$; unpacked vessel, average $k_{3/2} = (1.74 \pm 0.04) \times 10^{-4}$ torr$^{-1/2}$ s^{-1}; packed vessel, average $k_{3/2} = (1.73 \pm 0.02) \times 10^{-4}$ torr$^{-1/2}$ s^{-1}). At lower temperatures the agreement was less

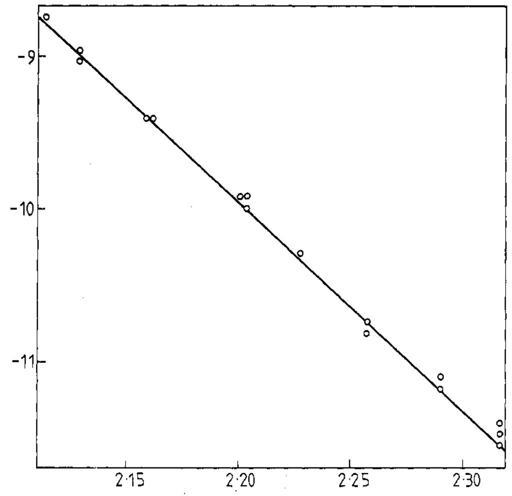


Figure 2. Arrhenius plot for $k_{3/2}$: (ordinate) ln ($k_{3/2}$/torr$^{-1/2}$ s^{-1}); (abscissa) $10^3K/T$.

satisfactory, despite vessel conditioning with hexamethyldisilazane. It appears that $k_{3/2}$ values in the "turn up" region of low $[Me_3GeH]_0/[I_2]_0$ are more sensitive to surface catalysis than the limiting $k_{3/2}$ values. Unfortunately because of the practical difficulty of cell design (for high surface-to-volume ratio, but with the necessary access to a light beam) ratios of $[Me_3GeH]_0/[I_2]_0$ of ≥ 50 were not practical in the packed vessel. The best that can be said is that rate constants $k_{3/2}$ at the lowest reliable temperature (431 K) were approximately a factor of 2 faster at $[Me_3GeH]_0/[I_2]_0 = 54$ although the trend with reactant ratios in the packed vessel suggests that the extrapolated limit would be much closer to that in the unpacked vessel. All this suggests that surface sensitivity is associated mainly with the region of lower reactant ratios. Although we cannot conclusively eliminate heterogeneous effects we shall assume that, where in the unpacked vessel a limiting low value for $k_{3/2}$ could be obtained, it may be associated with a homogeneous reaction.

The rate constants $k_{3/2}$ obtained in the unpacked vessel and at the high reactant ratio limit were fitted to the Arrhenius equation, a plot of which is shown in Figure 2. The linear least-squares line (431–474 K) gave

$$\log\,(k_{3/2}/\text{torr}^{-1/2}\ \text{s}^{-1}) = (9.18 \pm 0.10) - (117.5 \pm 0.9\ \text{kJ mol}^{-1})/RT \ln 10$$

where the error limits are one standard deviation.

To examine the inhibition phenomenon in more detail, a series of runs was performed in which HI was added initially to the reactant mixtures. This was to enhance the effect of inhibition and minimize any errors associated with the analysis. The iodine decay curves were now tested, as in previous work,[3-5] for consistency with the equation

$$-\frac{d[I_2]}{dt} = \frac{k_{3/2}[I_2]^{1/2}[Me_3GeH]}{1 + k'[HI]/[I_2]}$$

Runs were performed in the unpacked vessel using the following low pressures: I_2, ~0.25 torr; HI, 3–6 torr; and Me_3GeH, 9–43 torr. The ratio $[Me_3GeH]_0/[I_2]_0$ was thus kept high, at the expense of allowing more flexibility in starting conditions. Using the above-determined values for $k_{3/2}$ data were fitted as described previously[3,5] in the temperature range 436–474 K. All values of k' lay within the range 0.10 ± 0.01 and an Arrhenius plot yielded

$$\log k' = (-0.62 \pm 0.18) - (3.3 \pm 1.6\ \text{kJ mol}^{-1})/RT \ln 10$$

Because of the difficulties described earlier, no runs were performed in the packed vessel.

Reaction Mechanism and Bond Dissociation Energy

The observed kinetics are clearly complicated by surface effects but the residual homogeneous three-halves-order process, obeyed under the limited conditions described, parallels closely those of other iodination systems.[3-7] Thus the following iodine-atom abstraction chain mechanism seems the most likely:

$$I_2\ (+M) \rightleftarrows 2I\cdot\ (+M)\quad K_{I_2}$$

$$I\cdot + Me_3GeH \underset{2}{\overset{1}{\rightleftarrows}} Me_3Ge\cdot + HI$$

$$Me_3Ge\cdot + I_2 \xrightarrow{3} Me_3GeI + I\cdot$$

A stationary state treatment of this mechanism gives

$$-\frac{d[I_2]}{dt} = \frac{k_1K_{I_2}^{1/2}[I_2]^{1/2}[Me_3GeH]}{1 + k_2[HI]/k_3[I_2]}$$

Comparison with the experimental results reveals that both the orders of reaction and inhibition effect are fully accounted for. In addition, $k_{3/2}$ can be identified with $k_1K_{I_2}^{1/2}$ and k' with k_2/k_3. From the known values of $K_{I_2}^{1/2}$ the following expression for k_1 is obtained:

$$\log\,(k_1/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = (9.94 \pm 0.10) - (45.3 \pm 0.9\ \text{kJ mol}^{-1})/RT \ln 10$$

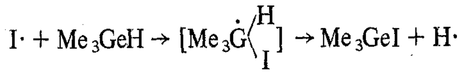
From the Arrhenius data for k' it follows that $E_2 - E_3 = 3.3 \pm 1.6$ kJ mol^{-1}. It seems reasonable to suppose that $E_3 = 0$ since alkyl radicals react with I_2 with no activation energy[7] and the reactions of germyl (by analogy with silyl) are more exothermic than those of alkyl radicals (see however the discussion on this point). Hence $E_2 = 3.3 \pm 1.6$ kJ mol^{-1}, and $\Delta H°_{1,2}(453\ \text{K}) = E_1 - E_2 = 42.0 \pm 1.8$ kJ mol^{-1}.

The correction of $\Delta H°(T)$ to room temperature requires use of $\Delta\bar{C}_p°$ (or the enthalpy function $H°(T) - H°(298)$) Both these quantities are unknown for the reaction step (1,2) because of lack of structural information concerning the $Me_3\dot{G}e$ radical (primarily its internal rotation barriers). However, $\Delta\bar{C}_p°$, although uncertain, is likely to be small (between +4 and −4 J K^{-1} mol^{-1}) and, therefore, we neglect this correction and assume $\Delta H°_{1,2}(298\ \text{K}) = \Delta H°_{1,2}(453\ \text{K})$. Since $\Delta H°_{1,2} = D(Me_3Ge\text{–}H) - D(H\text{–}I)$, then from the known value of $D(H\text{–}I) = 298$ kJ mol^{-1} hence $D(Me_3Ge\text{–}H) = 340$ kJ mol^{-1}. The statistical scatter of results leave an uncertainty of only ±2 kJ mol^{-1} (68% confidence level). However, in view of the assumptions made it seems that ±10 kJ mol^{-1} represent more realistic error margins (see Discussion).

Discussion

Despite the uncertainties in the data, the kinetics found for this reaction offer strong support for the atomic chain mechanism proposed. As well as the rate law agreement, the relatively high A factor for step (1), viz. $10^{9.94}$ dm^3 mol^{-1} s^{-1}, is in general accordance with expectations for H-atom abstractions by I.[7] A particular comparison with the reactions I· + Me_3CH[7] ($A = 10^{10.9}$ dm^3 mol^{-1} s^{-1}) and I· + Me_3SiH[3] ($A = 10^{11.1}$ dm^3 mol^{-1} s^{-1}) suggests that while the order of magnitude is correct, perhaps the A factor for this reaction may be slightly low. A slight residual surface contribution to reaction would cause lowering of both A and E.

An alternative and plausible I atom chain mechanism involves the displacement step



$$\mathrm{I\cdot + Me_3GeH \rightarrow \left[Me_3\dot{G}\begin{smallmatrix} /H \\ \backslash I \end{smallmatrix}\right] \rightarrow Me_3GeI + H\cdot}$$

Although this would fit the observed rate expression, it seems unlikely on two grounds. First, the intermediate five coordinate complex would almost certainly lose a methyl radical in preference to an H atom, thus leading to MeI as a major product, which was not found. Secondly, the *A* factor is expected to be low for such a process by analogy with a value of $10^{8.2}$ dm^3 mol^{-1} s^{-1} for the authentic displacement reaction[19,20]

$$\mathrm{I + Me_3SiSiMe_3 \rightarrow Me_3SiI + Me_3\dot{S}i}$$

Bond dissociation energies determined by this method are usually among the most reliable and so it is important to assess the most likely causes of uncertainty in the result determined here. These are twofold. First, as argued above, a small residual surface contribution to reaction might lead to lowering of A_1 and E_1. For the reasons outlined above, A_1 is not likely to be in error by more than a factor of $10^{0.9}$. The corresponding maximum error in E_1 and, therefore, D(Me$_3$Ge–H) is 8 kJ mol^{-1}. The second point concerns the magnitude of E_2. This has been argued to be 3 kJ mol^{-1} in the present system. However, the following argument suggests that this value might be an underestimate. Recent VLPP (very low pressure pyrolysis) work by Rossi and Golden[21] has shown by direct study that for the reactions of allyl and benzyl radicals with HI, the activation energies are 17 and 13 kJ mol^{-1}, respectively. This technique has not yet been applied to reactions of alkyl radicals with HI but the self-consistency of derived thermochemical data[2,7] suggests that experimental values of 6 ± 4 kJ mol^{-1} are unlikely to be in serious error. The point here is that the radicals, *whose reactions with HI are the least exothermic*, have the highest activation energies, and that a trend of activation energy within hydrocarbon radicals appears to exist.[28] It may be that there is no parallel between hydrocarbon and germyl radicals but, in terms of exothermicity in reaction with HI, Me$_3$Ge is more like an allyl or benzyl radical than an alkyl radical. Thus the possibility of a value of E_2 as high as 17 kJ mol^{-1} cannot be ruled out. In this case D(Me$_3$Ge–H) = 340 kJ mol^{-1} would be overestimated by 14 kJ mol^{-1}. It seems reasonable on these two grounds to propose error limits of ±10 kJ mol^{-1} on our value.

There has been no previous direct determination of D(Me$_3$Ge–H) with which to compare our result. As mentioned in the Introduction, Austin and Lampe[9] have inferred a value of 264 kJ mol^{-1} from their estimated activation energy for H-atom abstraction by H. For the reasons given this cannot be regarded as reliable. There remain arguments by analogy which are discussed below and which tend to offer support for our measured value. Jackson[8] derived a value for D(Me$_3$Ge–H) on the assumption that the difference between D(Me$_3$Si–H) and D(Me$_3$Ge–H) would be the same as the difference between the mean thermochemical bond energies of SiH$_4$ and GeH$_4$. At that time a value of D(Me$_3$Si–H) = 339 kJ mol^{-1} gave D(Me$_3$Ge–H) = 305 kJ mol^{-1} by this argument.[8] However, D(Me$_3$Si–H) is now known[3] to be close to 378 kJ mol^{-1} and, therefore, this argument now yields D(Me$_3$Ge–H) = 344 kJ mol^{-1} very close to the experimental value derived here.

Hosaka and Rowland[11] have shown from hot T atom abstraction studies that in silanes Si–H bond dissociation energies are not very sensitive to methyl substitution. Existing data from other sources give D(SiH$_3$–H) between 369[22] and 397[23] kJ mol^{-1} and D(Me$_3$Si–H) = 377 kJ mol^{-1} (ref 3) which supports this argument. Thus one might anticipate a similar situation for germanes. Therefore, the value of D(H$_3$Ge–H) is of interest. Saalfeld and Svec[24] derived 365 kJ mol^{-1} for this from electron impact measurements while Reed and Brauman[25] have set an upper limit of 386 kJ mol^{-1} from photoelectron detachment studies. Probably the most reliable value comes from measurements of the limit of HF vibration–rotation excitation in infrared chemiluminescence studies of F + GeH$_4$ by Setser and co-workers.[12] They have obtained a published value of ≤326 kJ mol^{-1} for D(H$_3$Ge–H) although this has been recently revised upward[26] to 338 kJ mol^{-1}. This is also in good accord with our value.

Further studies with germanes are planned and the further implications of this work for gas phase studies involving germanium compounds will be discussed elsewhere.[27]

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