

On the Role of the Solid–Gas Interface in the Thermolysis of Trimethylgermane and Trimethylstannane

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Metal film surfaces have a profound effect on the thermal decomposition of Me_3MH ($\text{M} = \text{Ge}$ and Sn), both of which unusually decompose by half-order kinetics at elevated temperature.

It is becoming increasingly apparent that in the formation of thin films by chemical vapour deposition (CVD), the predeposition chemistry occurring in the gas phase and/or at the solid–gas interface between the substrate and the gas phase can be of critical importance in determining the nature and characteristics of the resulting film.¹ For Group 4B elements many compounds of silicon, germanium and tin have been employed in the CVD deposition of element-containing films. However, whereas the mechanisms operating in the gas-phase thermolysis of organosilanes have been studied extensively² (although usually employing flow reactor techniques thereby suppressing any effects due to the reactor wall), little is known concerning the gas-phase chemistry of the heavier Group 4 congeners. As we have shown previously,³ FTIR spectroscopy may be employed to study MOCVD (metal–organic CVD) predeposition chemistry directly at the elevated temperatures involved (up to 873 K), and here we show how this technique can yield a large amount of information concerning the predeposition chemistry of the formation of germanium and tin films using trimethylgermane and trimethylstannane as precursor molecules.

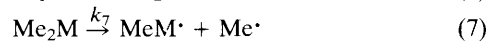
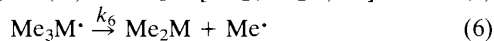
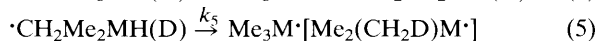
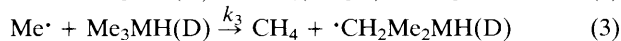
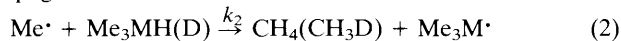
Decomposition of trimethylgermane at an appreciable rate begins at 673 K, whereas the onset of decomposition for the corresponding stannane is much lower (378 K). In both cases a metallic film is deposited on the walls of the IR cell and methane is the only hydrocarbon product observed. The other products are hexamethyldigermene in the case of Me_3GeH and tetramethyltin in the case of Me_3SnH . Deuteration studies using the corresponding trimethylmetal deuterides, Me_3MD ($\text{M} = \text{Ge}, \text{Sn}$) show that deuterium is only incorporated in $[\text{D}_2\text{H}_2]$ methane although unlabelled methane and, quite surprisingly, transient trimethylmetal hydride is also formed in addition to the metal-containing products observed in the decomposition of the hydrides (Fig. 1). This observation demonstrates unequivocally that abstraction of hydrogen by $\text{Me}_3\text{M}^\cdot$ radicals from methyl groups occurs as well as abstraction of hydridic hydrogen from the metal, and shows further that the reaction scheme proposed previously⁴ for the thermolysis of trimethylgermane is inadequate.

Monitoring the integrated band intensity of the metal–hydride $\nu(\text{M–H})$ stretching mode (2040 cm^{-1} in Me_3GeH and 1844 cm^{-1} in Me_3SnH both with P, Q and R fine structure) for

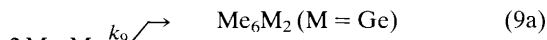
Initiation:



Propagation:



Termination:



Scheme 1

time-resolved spectra in the temperature ranges 673–873 K (M = Ge) and 378–503 K (M = Sn) shows that the rate of reaction is half-order with respect to the metal hydride (Fig. 2). Half-order rate constants ($\text{mol}^{1/2} \text{dm}^{-3/2} \text{s}^{-1}$) varied in the ranges 0.16×10^{-6} at 673 K to 69.7×10^{-6} at 773 K (M = Ge) and 0.17×10^{-5} at 378 K to 6.36×10^{-5} at 503 K (M = Sn). Significantly, a single experiment performed with trimethylsilane at 863 K (the limit of the apparatus) showed half-order kinetics in this case also ($k = 7.24 \times 10^{-6} \text{mol}^{1/2} \text{dm}^{-3/2} \text{s}^{-1}$). A mean value of 1.37 for the primary kinetic isotope effect $k_{\text{H}}/k_{\text{D}}$ was observed in the case of trimethylstannane. Arrhenius plots yielded values of the activation energy, E_{A} (kJ mol^{-1}), of 260 (Me_3GeH), 44.4 (Me_3SnH) and 46.1 (Me_3SnD).

The product distribution observed during the thermolyses of $[\text{H}_0]$ - and $[\text{H}_2]$ -trimethyl-germane and -stannane are consistent with the free-radical chain process shown in Scheme 1. Product distribution studies (M = Ge) and the reaction kinetics (M = Sn) dictate that the termination step [reaction (10)] does not occur or occurs only to a very low extent, and



bimolecular termination as observed for Group 4B radicals in solution⁵ is considerably more likely. The scheme successfully accounts for the formation of methane, monodeuteriomethane and transient Me_3MH observed during the thermolysis of the Me_3MD isotopomers. Corroboration that the reactions proceed *via* a free-radical mechanism is provided by inhibition in the presence of nitric oxide and catalysis by methyl iodide. In view of the magnitudes of the bond dissociation energies involved [$E_{\text{D}}(\text{M}-\text{H})$: *ca.* 343 kJ mol^{-1} (M = Ge), *ca.* 309 kJ mol^{-1} (M = Sn); $E_{\text{D}}(\text{M}-\text{Me})$: *ca.* 318 kJ mol^{-1} (M = Ge), *ca.* 272 kJ mol^{-1} (M = Sn)],⁶ it is most probable that the initiation step involves initial M–C rather than M–H bond rupture.

Furthermore, assuming steady-state conditions, from this reaction scheme may be derived the kinetic rate equation (11),

$$-d[\text{Me}_3\text{MH}]/dt = 3k_6(k_1/k_9)^{1/2} [\text{Me}_3\text{MH}]^{1/2} \quad (11)$$

fully consistent with the experimental data. Half-order reactions are quite rare. However, it is interesting to note that half-order kinetics have recently also been observed for the thermal decomposition of $\text{PtMe}_2(\text{MeNC})_2$ at 523 K, although no reaction scheme was presented which accounted for these observations.⁷

The derived rate equation indicates that the activation energy, E_{A} , is a composite involving the three processes (1), (6) and (9), which would predict an activation energy for the

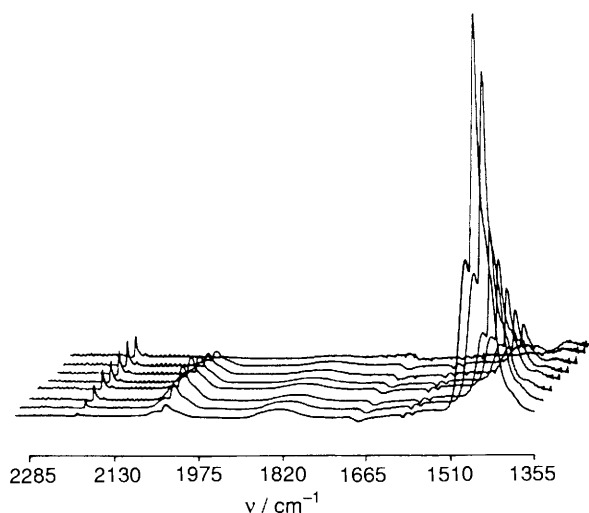


Fig. 1 Time-resolved IR spectra showing the formation of CH_3D [$\nu(\text{C}-\text{D})$ at 2200 cm^{-1}] and transient Me_3GeH [$\nu(\text{Ge}-\text{D})$ at 2040 cm^{-1}] during the thermolysis of Me_3GeD at 733 K [time axis varies from 0 (front) to 4200 (rear) s]

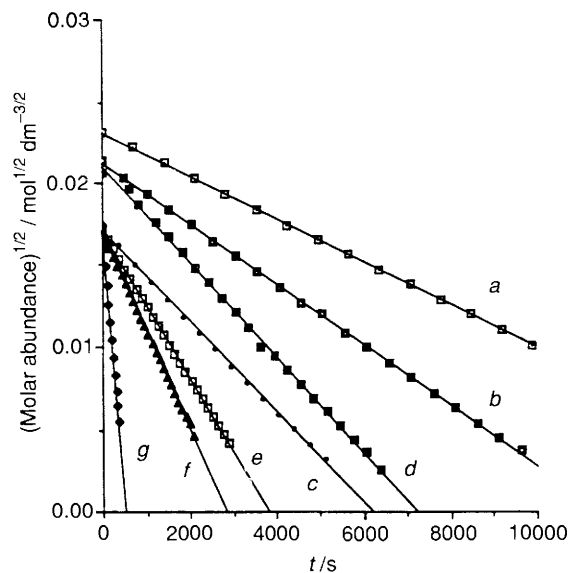


Fig. 2 Half-order rate plots for the decomposition of Me_3SnH at (a) 388 K, (b) 398 K, (c) 408 K, (d) 418 K, (e) 428 K, (f) 438 K and (g) 503 K

overall reaction of $[E(6) + \frac{1}{2}E(1) - \frac{1}{2}E(9)]$. Since radical termination generally occurs with very small or zero activation energy, the third term in this expression may be neglected. $E(1)$ and $E(6)$ may be substituted, respectively, by $E_{\text{D}}(\text{HMe}_2\text{M}-\text{Me})$ and $E_{\text{D}}(\text{Me}_2\text{M}-\text{Me})$, and hence the expression for E_{A} reduces to eqn. (12). In the case of M = Ge, estimating

$$E_{\text{A}} = E_{\text{D}}(\text{Me}_2\text{M}-\text{Me}) + \frac{1}{2}E_{\text{D}}(\text{HMe}_2\text{M}-\text{Me}) \quad (12)$$

the value of $E_{\text{D}}(\text{Me}_2\text{Ge}-\text{Me})$ to be of the order of 200 kJ mol^{-1} ,⁸ and that of $E_{\text{D}}(\text{HMe}_2\text{Ge}-\text{Me})$ as 318 kJ mol^{-1} ,⁶ then a value of *ca.* 359 kJ mol^{-1} for E_{A} might be expected. That this is not the case, and the observed value of E_{A} is only 260 kJ mol^{-1} , would suggest that some additional phenomenon is affecting either the magnitudes of $E_{\text{D}}(\text{Me}_2\text{M}-\text{Me})$ and/or $E_{\text{D}}(\text{HMe}_2\text{M}-\text{Me})$. In the case of Me_3SnH , the situation is even more disparate, with an observed activation energy of only 45 kJ mol^{-1} [*cf.* values of 180 kJ mol^{-1} for $E_{\text{D}}(\text{Me}_2\text{Sn}-\text{Me})$ ⁷ and 270 kJ mol^{-1} for $E_{\text{D}}(\text{HMe}_2\text{Sn}-\text{Me})$,⁶ giving a predicted activation energy of *ca.* 315 kJ mol^{-1}]. The most obvious process which may account for such a large perturba-

tion in the values of the bond dissociation energies is an interaction with the available surface (*i.e.* the metallic film coating the walls of the IR cell) presented to the gas-phase reactant. This would have the effect of weakening the metal–ligand bonds and hence the apparent magnitudes of the bond dissociation energies. That the observed effect is relatively small in the case of Me₃GeH but very large in the case of Me₃SnH would serve to suggest that the reactivity of Me₃SnH under these conditions is dominated by solid–gas interface effects whereas for Me₃GeH principally gas-phase processes occur.

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