Kinetics and Mechanism of the Thermolysis of Tetramethyltin in the Presence of Oxygen

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Fourier transform i.r. spectroscopy has been employed to study the kinetics and mechanism of the oxidative thermolysis of tetramethyltin in the temperature range 553—613 K.

Films of tin(IV) oxide deposited on glass by metal–organic chemical vapour deposition (MOCVD) methods exhibit characteristics which are extremely useful in several industrial contexts. However, in spite of the multiplicity of application of such films, little is known about the fundamental chemical reactions which occur during the deposition process, and previous work appears to have concentrated solely on determining the optimum conditions for film growth and quality.[1] Moreover, speculation concerning the reaction mechanism has resulted in controversy, with two principal modes of reaction being postulated: (i) a homogeneous process whereby the oxidative thermolysis of the precursor molecule takes place in the gas phase leading to a fine particulate of tin(IV) oxide, which is then deposited on the surface of the substrate, and (ii) a heterogeneous process, in which chemisorption of the molecule on the surface of the substrate occurs initially, with subsequent decomposition of the surface-adsorbed organotin species to the oxide. No-one as yet appears to have addressed the problem of studying the reactions which must necessarily occur during the transformation of the molecular precursor into the resultant oxide film. In this communication we describe how Fourier transform i.r. spectroscopy may be utilised in the study of the chemistry of such systems using the oxidative thermolysis of tetramethyltin as an example. This reaction has always been assumed to proceed with total oxidation of tetramethyltin, *i.e.* according to equation (1).

$$\mathrm{Me_4Sn + 8O_2 \rightarrow SnO_2 + 6H_2O + 4CO_2} \qquad (1)$$

The experimental arrangement comprised an i.r. gas cell surrounded by a thermostatically controlled heater and connected to a conventional vacuum line system operating at a backing pressure of $<10^{-5}$ mbar. Gas-phase concentrations of the reactant and products were measured by observing the absorbance changes in i.r. bands characteristic of each component [*e.g.* ν(Sn–C) and ρ($SnCH_3$) for tetramethyltin] and calibrated using known concentrations.

Reaction of mixtures containing a 9 : 1 oxygen : tetramethyltin molar ratio [*i.e.* slightly more oxygen than required for exhaustive oxidation according to equation (1)] in the temperature range 553—613 K gave as the gaseous reaction products methane (*ca.* 3 mol) and carbon dioxide (*ca.* 1 mol) per mol of tetramethyltin, *i.e.* the reaction proceeds according to the less, though still thermodynamically favourable, stoicheiometry of equation (2). Traces of carbon

$$\mathrm{Me_4Sn + 2O_2 \rightarrow SnO_2 + 3CH_4 + CO_2} \qquad (2)$$

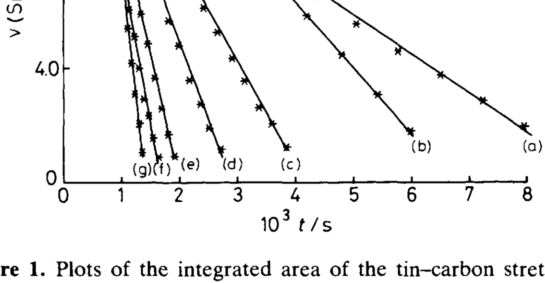

Figure 1. Plots of the integrated area of the tin–carbon stretching vibration *vs.* time at (a) 553, (b) 563, (c) 573, (d) 583, (e) 593, (f) 603, and (g) 613 K. Solid lines are the least squares best fit straight lines.

Table 1. Kinetic data for the thermal decomposition of tetramethyltin –oxygen mixtures.

Temp./K	$p(Me_4Sn)^a$/ mmHg	$p(O_2)/p(Me_4Sn)^b$	$10^8 k_{obs.}$/ ($mol\ dm^{-3}\ s^{-1})^c$
553	4.81	8.98	2.43
563	5.77	9.28	4.11
573	5.14	9.33	6.91
583	4.92	9.28	11.21
593	4.67	9.54	17.56
603	4.56	9.44	20.73
613	5.40	9.15	31.76

[a] Initial pressure of tetramethyltin (at 296 K). [b] Initial ratio of oxygen to tetramethyltin. [c] Correlation coefficients are in the range 0.9969—0.9999.

monoxide were also sometimes observed. Reaction was very slow below *ca.* 533 K. Concentrations of tetramethyltin and both the two gaseous products, methane and carbon dioxide, could be accurately and simultaneously obtained from time-resolved spectra, leading readily to the evaluation of rate constant data for each component. Plots of the absorbance of the tin–carbon stretching band *vs.* time at temperatures in the range 553—613 K are all linear from the commencement of isothermal conditions (Figure 1), *i.e.* under these conditions the reaction is zero-order in tetramethyltin in all cases. Reaction rates are also independent of oxygen concentration (*i.e.* the order with respect to oxygen is also zero-order). The onset of formation of methane and carbon dioxide coincides with the initiation of tetramethyltin reaction, and the rate of formation of both of these products similarly shows a zero-order dependence on tetramethyltin. Rate constants for the loss of tetramethyltin vary from 2.43×10^{-8} mol dm^{-3} s^{-1} at 553 K to 31.76×10^{-8} mol dm^{-3} s^{-1} at 613 K (Table 1).

The availability of rate constant data over a range of temperatures enables the thermodynamics of the reaction to be probed. In the present case the Arrhenius plot is linear, and least squares analysis gives the relationship (3), with a calculated activation energy, E_a, for the rate-determining step of the reaction of 114 and 116 kJ mol^{-1} from duplicate experimental data.

$$\ln k_{obs.} = 7.05 - 13.8 \times 10^3/T \qquad (3)$$

The accumulation of data obtained from the time- and temperature-resolved i.r. spectra allows conclusions to be derived regarding the mechanism of the reaction. The unexpected course of the reaction leading to the formation of methane shows that the reaction is under kinetic rather than thermodynamic control. Further, the order of reaction with respect to both reactants and products is zero, which, along with the low activation energy {*cf.* the tin–carbon bond dissociation energy, $D[(CH_3)_3Sn–CH_3]$ 278 kJ mol^{-1} for tetramethyltin}, indicates that the reaction is not a homogeneous gas-phase reaction, but rather a heterogeneous reaction which takes place on the walls of the reaction vessel. Thus, we conclude that dissociative chemisorption of tetramethyltin onto the surface of the glass i.r. cell occurs, with subsequent cleavage of methyl groups from tin and desorption of methane and carbon dioxide. It is inappropriate to speculate further on the mechanisms of the surface reactions at this stage. Suffice it to say that, once anchored to the surface, further reaction would be expected to occur readily as we have observed with other organic species on the surface of tin(IV) oxide.[2]

Thus, with this example we have demonstrated that Fourier transform i.r. spectroscopy can be a powerful tool for the investigation of the chemistry involved under typical conditions employed in MOCVD. Further, whilst we have employed the method for the study of tin(IV) oxide film formation, it has the potential of becoming a technique which is generally applicable to other systems.

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