Decomposition, Oxidation, and Hydrolysis Kinetics of Monobutyltintrichloride

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Due to its electrical, optical, and mechanical properties, tin oxide coatings can be found in a wide range of applications. Fluorine doped tin oxides are transparent for visible light, highly reflective for infrared radiation, and may have a sheet resistance down to 3 Ω/square. These thin films are used in architectural windows for reflecting heat [1], in solar cells for carrying the cell's current without blocking sun light [2], in wear resistive coatings on glass bottles [3], and in gas sensors [4]. The most common method for producing tin oxide coatings on glass is chemical vapour deposition (CVD). Although a wide variety of precursors can be used, one of the most commonly used is monobutyltintrichloride (MBTC). Tin oxide deposition from mixtures of MBTC, oxygen, and water vapor is a difficult process to optimize and control; low conversion efficiencies are often observed and good film uniformity can be difficult to obtain. Chemical reactions in the gas phase are known to be important, even rate controlling, in some tin oxide deposition processes. Consequently, the chemistry and kinetics of MBTC thermal decomposition, oxidation, and hydrolysis reactions in the gas phase is a critical element in model development. This paper focuses on analysing the gas-phase reactions occurring during deposition of tin oxide. The experiments are performed in a reactor system in which concentration and temperature distributions can be neglected, thus allowing analysis of the intrinsic chemical kinetics.

Using a continuously stirred tank reactor (CSTR) system equipped with an in-situ FTIR spectrometer the deposition of tin oxide from MBTC and O_2/H_2O was studied. Pyrolysis of MBTC is expected, based on thermodynamic arguments, to be initiated by the cleavage of the Sn-C bond. The overall activation energy measured in the CSTR experiments is 126 kJ mol^{-1}, which is considerably lower than the Sn-C bond energy of 289 kJ mol^{-1} predicted by *ab initio* calculations. We attribute this to low-activation-energy reactions in which Cl and H radicals attack MBTC subsequent to the initiation step, which accelerates the decomposition. The principal decomposition products are $SnCl_2$, C_2H_4, HCl, with minor amounts of 1-C_4H_8 and CH_4. Tin-containing species are not observed directly, although condensed $SnCl_2$ is found in the exhaust system of the reactor. The products are consistent with the known decomposition kinetics of the C_4H_9 fragment of MBTC and the expected decomposition of $SnCl_3$ to $SnCl_2$ + Cl following initial cleavage of the Sn-C bond.

Deposition of tin oxide from MBTC/oxygen mixtures is observed to occur at temperatures as low as 673 K, well below the temperature at which MBTC begins to decompose. Since direct gas-phase reaction between MBTC and oxygen is not expected, this experimental result is an indication that deposition occurs via surface reactions at these low temperatures (< 723 K).

The tin oxide growth rate from MBTC/O_2 mixtures is dramatically increased by adding water to the precursor mixture. Although *ab-initio* and equilibrium calculations show that water easily reacts with tin-intermediates such as $SnCl_2$ or $SnCl_3$, computational modelling of the CSTR indicates that these reactions do not lead to higher conversion rates of MBTC. Another possibility is that H_2O forms OH sites on the surface, which can easily abstract Cl from the eventual film precursor or even MBTC.

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