

# The gas phase thermolysis and oxidative thermolysis of some homoleptic tetraalkylstannanes: an FT-IR study

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## Abstract

Fourier transform infrared spectroscopy has been employed to investigate the thermal decomposition chemistry of a number of homoleptic tetraorganostannanes,  $R_4Sn$  ( $R = Et, nPr, nBu, sBu$ ) in the temperature range 543–573 K. Neat tetraethyltin and tetra-*n*-butyltin give principally alkene (ethene when  $R = Et$ ; a mixture of but-1-ene and *cis*- and *trans*-but-2-ene when  $R = nBu$ ) with some of the corresponding alkane. When the thermolysis reactions are carried out in the presence of oxygen decomposition of all the tetraalkylstannanes studied give alkene and an organic carbonyl compound, together with carbon dioxide and water. In the cases of tetra-*n*-propyltin, tetra-*iso*-propyltin and tetra-*sec*-butyltin, propanal, acetone, and butanone, respectively, are formed as the tetraorganotin is consumed. Only small amounts of carbonyl compounds are formed initially in the thermal decomposition of tetraethyltin and tetra-*n*-butyltin in the presence of oxygen, alkenes being the major product, although in the latter case peaks due to butyraldehyde grow in intensity as the reaction mixture is held at 573 K. The decompositions in both the absence and presence of oxygen are considered to proceed by radical mechanisms involving the homolytic fission of the tin-carbon bond to produce alkyl radicals, which react to give the observed products.

**Keywords:** Thermolysis; Pyrolytic oxidation; Tin; Infrared; Pyrolysis; Tetraalkylstannanes

## 1. Introduction

We have previously shown that the oxidative thermolysis of tetramethyltin [1] and dimethyldivinyltin [2] proceed via a surface-mediated process in which the initial step is dissociative chemisorption of the organostannane at the available solid-gas interface, followed by further reaction of the adsorbed species. The reaction is of zero order in respect to the disappearance of the stannane and the reaction rate was observed to be sensitive to the magnitude of the surface area. Gas phase products are methane and carbon dioxide. In contrast, in the absence of oxygen, the thermal decomposition of tetramethyltin is considered to proceed via tin-carbon bond homolysis with first order kinetics giving methane, ethane and ethene [3,4]. The thermolysis of tetraethyltin is similar [5]. Because additional reaction pathways are available when  $\beta$ -hydrogen atoms are available on the alkyl chain, we have now

examined the thermal behaviour of a number of homoleptic tetraalkylstannanes in both the presence and absence of a small amount of oxygen.

## 2. Experimental details

Thermal decomposition studies were carried out using a stainless steel infrared gas cell of diameter 19 mm and length 100 mm equipped with silver chloride windows. A gas-tight seal was effected with a knife-edge seal using a silver metal gasket. The cell was connected to a conventional vacuum system (backing pressure  $< 10^{-4}$  torr). The organotin compound to be studied was contained in a stainless-steel reservoir situated adjacent to the infrared cell. For the organotin compounds of lower volatility, the reservoir was heated to 430 K in order to obtain an appropriate vapour pressure of compound in the cell. In a typical decomposition run at 573 K, the spectra were recorded at intervals of one minute using 10 scans per spectrum (spectral recording time 14–15 s. All data were recorded at

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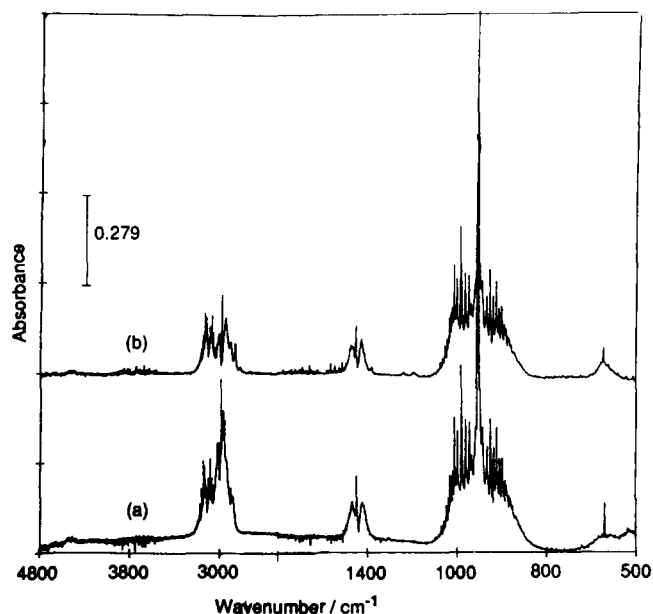


Fig. 1. Infrared spectra of (a) the reaction products from the thermolysis of neat tetraethyltin at 573 K and (b) ethene.

a resolution of 2 cm<sup>-1</sup>. In the reactions with oxygen, the organotin compound was first introduced into the preheated infrared cell and the oxygen then added. Spectra were usually recorded approximately every 30 s.

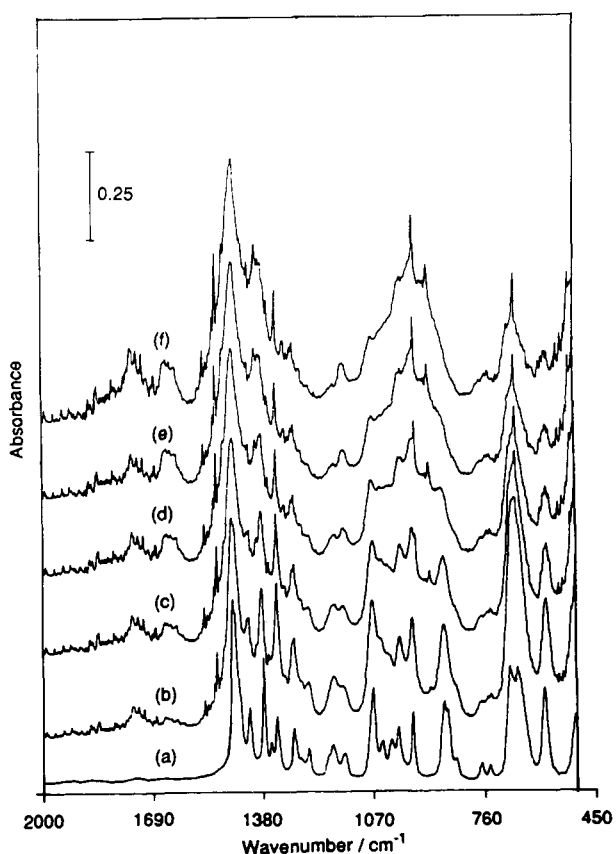


Fig. 2. Infrared spectra of neat tetra-*n*-butyltin at (a) 573 K; (b) after 7.5 min; (c) 10.5 min; (d) 15.5 min; (e) 19 min; (f) 22 min at 573 K.

### 3. Results

#### 3.1. The thermolysis of neat tetraalkylstannanes

##### 3.1.1. Tetraethyltin

When tetraethyltin (ca. 5 torr) was heated at 573 K all the characteristic bands at 2920, 2880, 2840, 2795, 1457, 1449, 1412, 1367, 1224, 1178, 1003, 950, 936, 661, 658, 497 cm<sup>-1</sup> broadened and reduced in intensity. Simultaneously, new bands arose at 950 cm<sup>-1</sup> ( $\delta(\text{CH}_2)_{\text{wag}}$ ) and 1443 cm<sup>-1</sup> ( $\delta(\text{CH}_2)_{\text{sciss}}$ ) due to ethene (Fig. 1). No tetraethyltin was present at the end of the reaction. Although the major product from the thermolysis was ethene, spectral subtraction showed that some ethane was also formed.

##### 3.1.2. Tetra-*n*-butyltin

On heating tetra-*n*-butyltin in the gas phase at 573 K the characteristic bands at 1461, 1416, 1378, 1338, 1291, 1072, 1000, 959, 871, 701, 686, 592, and 503 cm<sup>-1</sup> (Fig. 2(a)) slowly decayed in intensity and were replaced by a complex spectrum (Fig. 2(b–f)). Inspection of the final spectrum (Fig. 2(f)) showed it to be largely composed of bands due to butane (maxima around 1461 and 1370 cm<sup>-1</sup>), *cis*-but-2-ene (670 cm<sup>-1</sup>), *trans*-but-2-ene (975 cm<sup>-1</sup>), and but-1-ene (914 cm<sup>-1</sup>).

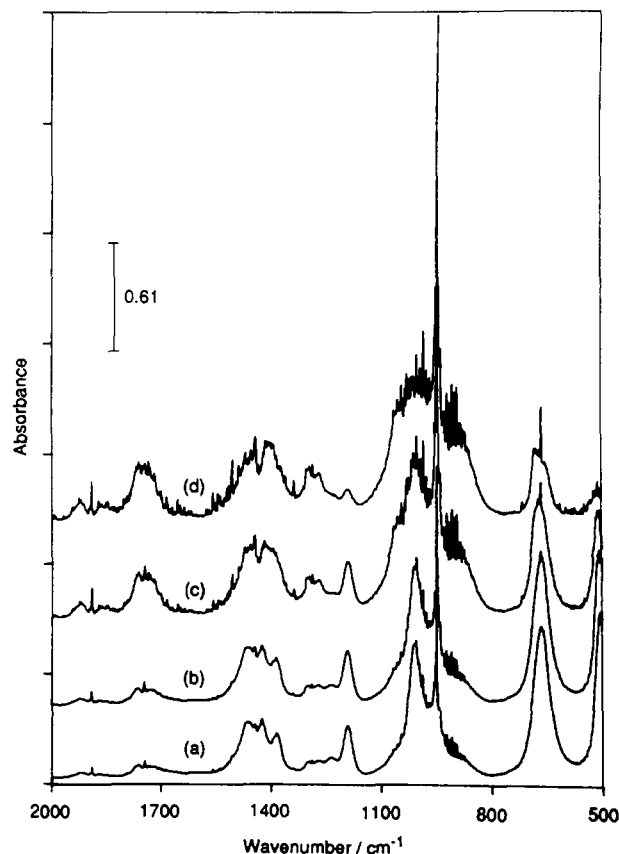


Fig. 3. Infrared spectra of a tetraethyltin oxygen mixture at 543 K (a), and the same mixture after (b) 10 mins; (c) 20 mins; (d) 42 mins at 543 K.

### 3.2. The oxidative thermolysis of tetraalkylstannanes

#### 3.2.1. Tetraethyltin

Ethene is also the major product when tetraethyltin is heated at 543 K in the presence of oxygen. However, small quantities of additional products are also formed including carbon dioxide ( $688\text{ cm}^{-1}$  ( $\delta(\text{CO}_2)$ )), acetaldehyde ( $1745\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$ )), and water vapour (rotational fine structure in the range  $1300\text{--}2000\text{ cm}^{-1}$ ) (Fig. 3). Again small quantities of ethane are also probably produced.

#### 3.2.2. Tetra-*n*-propyltin

Fig. 4 shows the spectral changes when tetra-*n*-propyltin is heated in the gas phase at 553 K in the presence of oxygen. At the start of the reaction (Fig. 4(a)) the spectrum already shows a number of new bands in addition to those of tetra-*n*-propyltin. Bands due to propene (characteristic bands at 909 and 991  $\text{cm}^{-1}$ ) propanaldehyde ( $\nu(\text{C}=\text{O})$  at  $1748\text{ cm}^{-1}$ ) and water vapour all increase as the reaction proceeds. No tetra-*n*-propyltin remains after 60 mins.

#### 3.2.3. Tetra-*iso*-propyltin

In addition to the characteristic bands of tetra-*iso*-propyltin at 1463, 1381, 1367, 1200, 1151, 1080, 993,

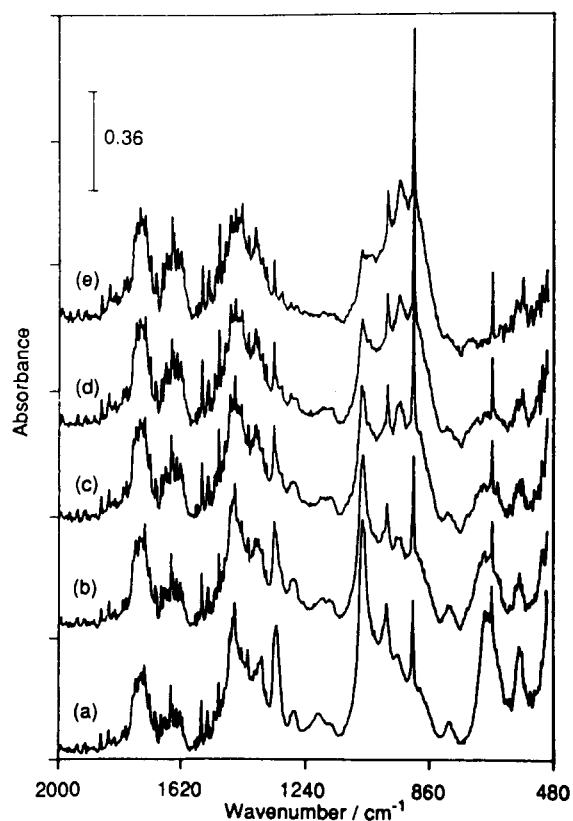


Fig. 4. Infrared spectra of a tetra-*n*-propyltin/oxygen mixture at 553 K (a), and the same mixture after (b) 5 min; (c) 20 min; (d) 35 min; (e) 60 min at 553 K.

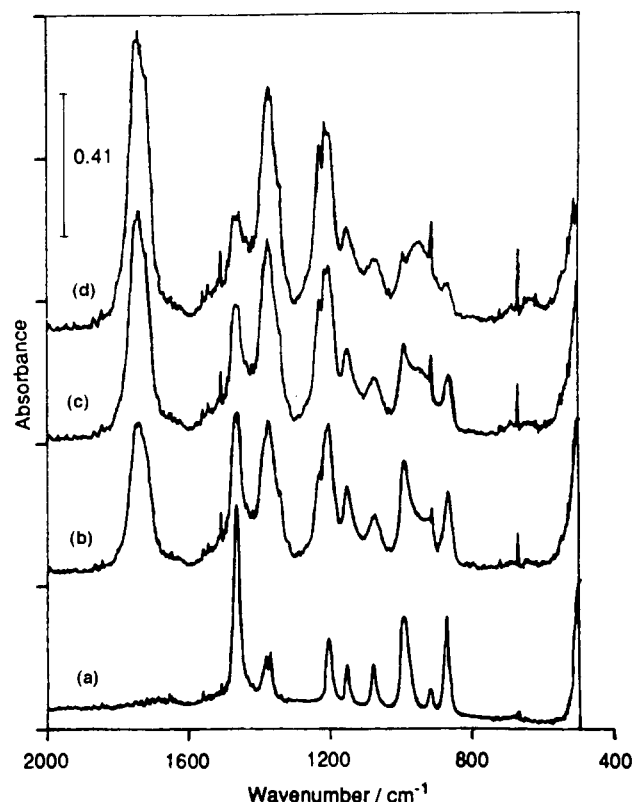


Fig. 5. Infrared spectra of a tetra-*iso*-propyltin/oxygen mixture at 573 K (a), and the same mixture after (b) 5 min; (c) 15 min; (d) 25 min at 573 K.

914, 870, 501  $\text{cm}^{-1}$ , several new bands are observed to grow in the reaction mixture at 573 K (Fig. 5). The new bands are readily attributable to acetone ( $1741\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$ ), 1366 and 1209  $\text{cm}^{-1}$ ), *iso*-propanol (1150, 1072  $\nu(\text{C}-\text{O})$  and 946  $\text{cm}^{-1}$ ), propene (909 and 991  $\text{cm}^{-1}$ ) and carbon dioxide (2340  $\text{cm}^{-1}$  and 668  $\text{cm}^{-1}$ ). All four products are present after 25 min, although not all the tetra-*iso*-propyltin is consumed at that stage. No other products appear to be formed.

#### 3.2.4. Tetra-*n*-butyltin

When a tetra-*n*-butyltin is heated at 573 K in the presence of oxygen rapid decomposition takes place to give a mixture of butane, but-1-ene, and *cis*- and *trans*-but-2-ene, carbon dioxide, water vapour and butyraldehyde ( $\nu(\text{C}=\text{O})$  at  $1745\text{ cm}^{-1}$ , aldehydic  $\nu(\text{C}-\text{H})$  at  $2723\text{ cm}^{-1}$ ) (Fig. 6). Further production of butyraldehyde, carbon dioxide, water vapour occurred. There was no firm evidence for the formation of butan-1-ol.

#### 3.2.5. Tetra-*sec*-butyltin

The major products formed in the oxidative thermolysis of tetra-*sec*-butyltin (characteristic bands at 1460, 1452 sh, 1377, 1368, 1336, 1291, 1182, 1132, 1100, 1078, 1025, 995, 962, 947, 836, 790, 770, 579, 534, 484, 445  $\text{cm}^{-1}$  were butanone (bands at 1752, 1730 ( $\nu(\text{C}=\text{O})$ ), 1373 and 1177  $\text{cm}^{-1}$ ), butane, *cis*- and *trans*-

but-2-ene, and water vapour (Fig. 7)). In addition, a small amount of butan-2-ol may be produced although positive identification is difficult since all of the major absorption bands occurring in regions of the spectra which contain other features. But-1-ene may also be present but in small amounts (very weak peak at  $914\text{ cm}^{-1}$ ).

#### 4. Discussion

The thermolysis of both neat tetraethyltin and tetra-*n*-butyltin at 573 K affords alkenes together with small amounts of the corresponding alkane as the only gas phase products. In the case of tetra-*n*-butyltin a mixture of *cis*-but-2-ene, *trans*-but-2-ene, and but-1-ene (but no butadiene) are formed. By analogy with the conclusions reached in previous studies on tetramethyltin, [1] tetra-*n*-butyltin [6], and trimethylgermane and -stannane [7], we rationalise these observations in terms of the sequential homolytic fission of the tin-carbon bonds according to Scheme I, whereby the corresponding alkyl radical is formed in high abundance. These radicals can then lose a hydrogen atom to form the alkene. In the case of the butyl radical iso-

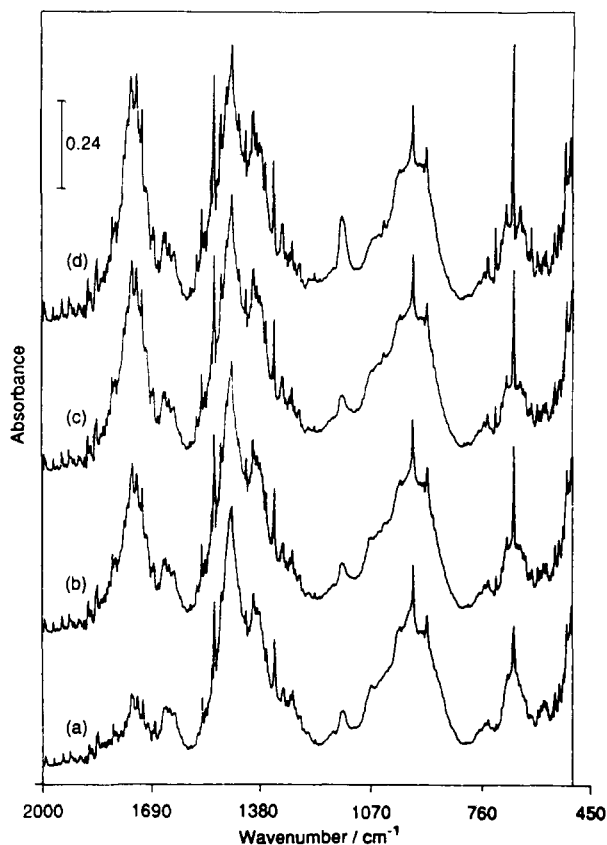


Fig. 6. Infrared spectra of a tetra-*n*-butyltin/oxygen mixture at 573 K (a), and the same mixture after (b) 23 s; (c) 46 s; (d) 12.5 min at 573 K.

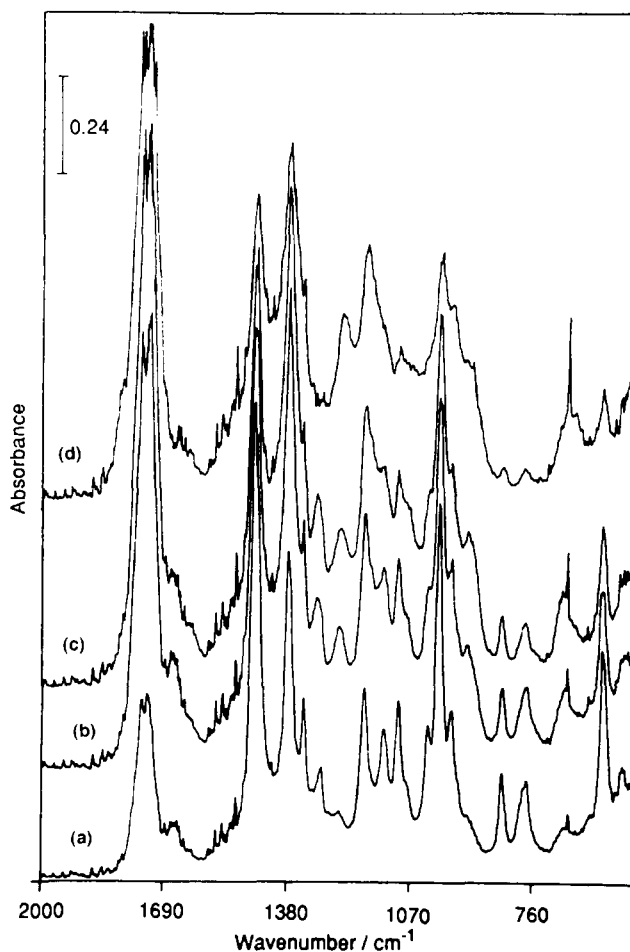


Fig. 7. Infrared spectra of a tetra-*sec*-butyltin/oxygen mixture at 573 K (a), and the same mixture after (b) 3 min; (c) 10 min; and (d) 25 min at 573 K.

merisation to the more stable secondary radical leads to the formation of the isomeric *cis*- and *trans*-but-2-enes in addition to but-1-ene. The small amounts of alkane also observed result either from the reaction of the alkyl radical with a hydrogen atom or from abstraction of a hydrogen atom the tetraalkyltin. Although not observable by IR spectroscopy it is highly probable that dihydrogen is also formed in the reactions through either hydrogen radical coupling or abstraction.

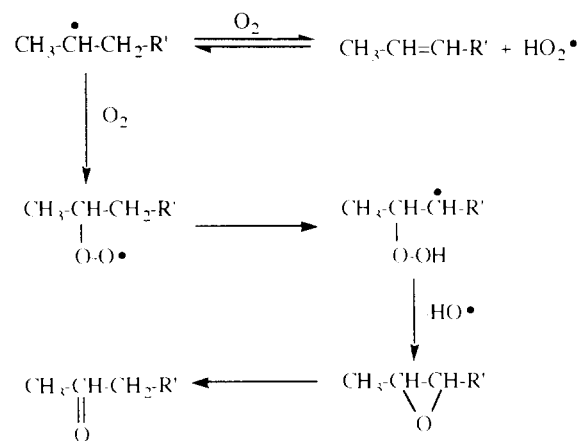
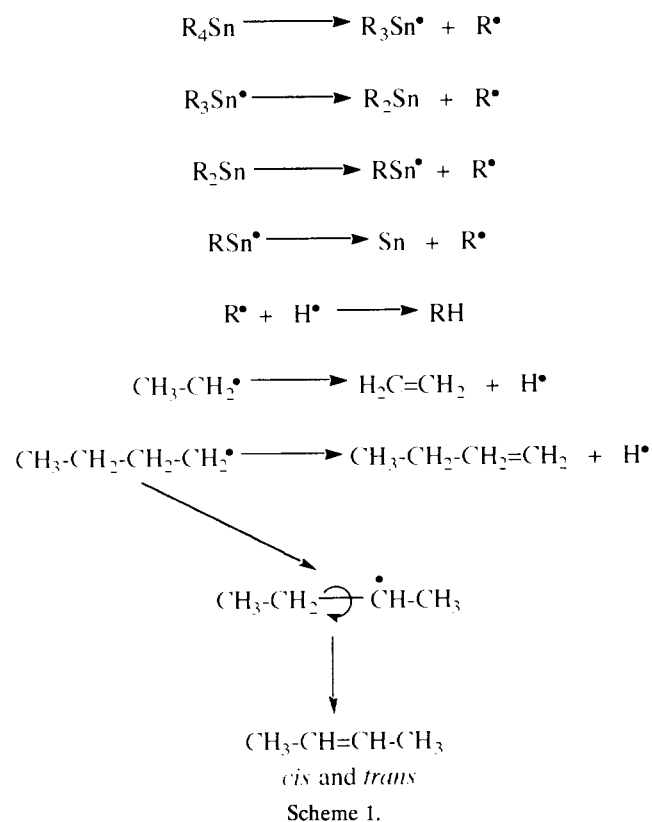
Alkenes are also formed when the thermolysis reactions are carried out in the presence of oxygen, but oxygen-containing products are also formed. The decomposition of all the tetraalkylstannanes studied in the presence of oxygen give alkene and an organic carbonyl compound, together with carbon dioxide and water. The results obtained in the present study are summarised in Table 1. In the case of tetra-*n*-propyltin, tetra-*iso*-propyltin and tetra-*sec*-butyltin, the spectra show quite clearly the formation of the corresponding organic carbonyl compound (propanal, acetone, and butanone, respectively) with the other gas phase

Table 1  
Summary of the products of the thermolysis of tetraalkyl-stannanes in the presence of oxygen

Organo-stannane / reaction temp. (K)	Products		
	Hydrocarbons	Oxygenated Organics	Others
Et <sub>4</sub> Sn/543	Ethene Ethane	Ethanol (?) Acetaldehyde	Carbon monoxide Carbon dioxide Water
<sup>n</sup> Pr <sub>4</sub> Sn/553	Propene Propane (?)	Propanal	Carbon dioxide Water
<sup>i</sup> Pr <sub>4</sub> Sn/573	Propene	Acetone Propan-2-ol	Carbon dioxide Water
<sup>n</sup> Bu <sub>4</sub> Sn/573	But-1-ene <i>cis</i> -But-2-ene <i>trans</i> -But-2-ene Butane	Butyraldehyde	Carbon dioxide Water
<sup>s</sup> Bu <sub>4</sub> Sn/573	<i>cis</i> -But-2-ene <i>trans</i> -But-2-ene	But-2-one	Carbon dioxide Water

products as the tetraorganotin is consumed. However, only small amounts of carbonyl compounds are formed initially in the thermal decomposition of tetraethyltin and tetra-*n*-butyltin in the presence of oxygen, alkenes being the major product, although in the latter case peaks due to butyraldehyde grow in intensity as the reaction mixture is held at 573 K.

Although there is little doubt that there is a contribution from the purely gas phase reaction pathway (Scheme 1), the product distribution and the facility



Scheme 2.

with which the reactions proceed in the presence of oxygen suggest that an alternative reaction pathway is available. We have previously demonstrated that the products of the oxidative thermolysis of tetramethyltin are methane and carbon dioxide and that there is transient formation of formaldehyde and methanol. The process by which these products are formed involves an initial dissociative chemisorption of tetramethyltin at the solid-gas interface followed by further reaction of the surface methoxy and trimethylstannyl species [2]. In addition, we have demonstrated that alkyl groups containing more than one carbon atom bound to tin atoms incorporated into the surface of tin(IV) oxide gel can follow two reaction pathways: (i) alkene elimination and desorption of the corresponding alkene, and (ii) oxidation to surface-bound carboxylate and carbonate [8]. In the former, increase in the Brønsted acidity of the surface was shown to facilitate isomerisation of C<sub>4</sub> alkenes. However, gas phase reactions of alkyl radical with oxygen are also well documented, and these indicate that the formation of alkenes and oxygen-containing organic products may be formed in purely homogeneous gas phase processes [9]. Although it is not possible unequivocally to distinguish between surface-mediated heterogeneous and a gas-phase homogeneous processes for the formation of the oxygen-containing products, we favour the latter since decomposition of the tetraalkylstannanes proceeds at the same temperature even in the absence of oxygen. The alkyl radicals produced (Scheme 1) may then react with oxygen by two pathways (Scheme 2): (i) to form the corresponding alkene, or (ii) to form the carbonyl compound via an intermediate epoxide. The formation of carbon dioxide and water may well proceed by a surface catalysed process, although again it is not necessary to invoke such a pathway.

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