# Photochemistry of Ethyltrimethylstannane and n-Propyltrimethylstannane at 185 nm

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Ethyltrimethylstannane vapour (*ets*) yields several gaseous hydrocarbons on photolysis together with a yellow polymer which deposits on the cell window. Addition of nitrogen or argon (130 mbar) reduces the yields by 90 % but there is a residual reaction which is unaffected by pressure of inert gas. Addition of oxygen reduces some yields to zero. The major primary reactions are

 $C_2H_5Sn(CH_3)_3+h\nu(\lambda = 185 \text{ nm})$ 

 $\rightarrow C_2H_4 + (CH_3)_3SnH, \ \phi \sim 0.40;$  $\rightarrow C_2H_5 + CH_3 + Sn(CH_3)_2, \ \phi \sim 0.55.$ 

The quantum yields of formation of the radical products are increased by radical abstraction from the stannane. Similar results were found for propyltrimethylstannane (pts) but the principal free radical reaction is

 $C_3H_7Sn(CH_3)_3 + hv(\lambda = 185 \text{ nm}) \rightarrow C_3H_7 + 2CH_3 + Sn(CH_3).$ 

The quenching effect is attributed to the deactivation of one of the two excited state precursors of the reaction.

This paper reports the second of two photochemical studies of the tetraalkyl-stannanes.

#### EXPERIMENTAL

The apparatus and technique was described previously.<sup>1</sup> Ethyltrimethylstannane (ets) was prepared by the reaction of  $C_2H_5MgI$  and  $(CH_3)_3SnCl$ . The chloride was prepared by refluxing  $(CH_3)_4Sn$  with  $SnCl_4$  for 4 h under nitrogen. ets was purified by fractional distillation and preparative gas chromatography. n-Propyltrimethylstannane (pts) was prepared in the same way.<sup>2</sup> The quantum yields of formation were determined with an ethylene actinometer.<sup>3</sup>

## RESULTS

The full results are deposited at Keele<sup>2</sup>; only a selection are reported here. Table 1 gives the yields of the gaseous products with their quantum yields. By using a filter, acetic acid (2 %) in water, it was shown that the photolysis occurred at 185 nm and that there was no sensitization. A deposit which formed on the window of the cell was found to be a polymer containing tin. Unlike the tetramethyl compound the deposit from *ets* contained no metallic tin.

# EFFECT OF IRRADIATION TIME AND INTENSITY

Polymer was deposited by photolysis of each compound and the rate of reaction decreased with time. The proportional decrease was the same for all the gaseous

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products. The rate was constant for the first 10 min and so subsequent kinetic runs were performed with 5 m irradiations. The windows were cleaned between each run. The intensity dependence was measured over a tenfold range and at  $25^{\circ}$ C all the rates were proportional to the intensity.

# TABLE 1.—PRODUCTS FROM THE PHOTOLYSES OF *ets* and *pts* together with THEIR YIELDS AND QUANTUM YIELDS

ets $p(ets) = 13 \text{ mbar}: t = 25^{\circ}\text{C}$		$p(pts) = 8 \text{ mbar}; t = 25^{\circ}\text{C}$	
yield/mol×108	quantum yield	yield/mol × 108	quantum yield
0.35	0.06	0.61	0.05
2.41	0.39	0.86	0.076
3.20	0.53	4.10	0.36
0	_	2.76	0.24
7.44	1.31	trace	
3.12	0.73	6.72	0.58
0	_	present but not analyzed	
0		not estimated	
	p(ets) = 13  mb yield/mol×108 0.35 2.41 3.20 0 7.44 3.12 0 0	$\begin{array}{c} ets\\ p(ets) = 13 \text{ mbar}; \ t = 25^{\circ}\text{C}\\ yield/mol \times 10^8  quantum yield\\ \hline 0.35 \qquad 0.06\\ 2.41 \qquad 0.39\\ 3.20 \qquad 0.53\\ 0 \qquad\\ 7.44 \qquad 1.31\\ 3.12 \qquad 0.73\\ 0 \qquad\\ 0 \qquad\end{array}$	$p(ets) = 13 \text{ mbar}$ ; $t = 25^{\circ}\text{C}$ $p(pts) = 8 \text{ mbar}$ $yield/mol \times 10^8$ quantum yield $yield/mol \times 10^8$ $0.35$ $0.06$ $0.61$ $2.41$ $0.39$ $0.86$ $3.20$ $0.53$ $4.10$ $0$ - $2.76$ $7.44$ $1.31$ trace $3.12$ $0.73$ $6.72$ $0$ -present but not estimate $0$ -not estimate

### EFFECT OF REACTANT PRESSURE

Fig. 1 and 2 show the effect on product yield of changing the pressure of either *ets* or *pts*. Within the pressure range all the incident light is absorbed so that the increases observed for all products are due to a kinetic effect which is first order in reactant concentration.



FIG. 1.—Variation of product yield with pressure of *ets.*  $t = 25^{\circ}$ C; ethane,  $\triangle$ ; ethylene,  $\bigcirc$ ; propane,  $\bigtriangledown$ ; butane, 0.



pressure/mbar

FIG. 2.—Variation of product yield with pressure of *pts.*  $t = 25^{\circ}C$ ; methane,  $\diamondsuit$ ; ethane,  $\bigcirc$ ; ethylene,  $\circlearrowright$ ; butane,  $\bigtriangleup$ .



FIG. 3.—Variation of ethylene yield from the photolysis of *ets* with pressure of added gas.  $p(ets) = 13 \text{ mbar}; t = 25^{\circ}\text{C};$  nitrogen,  $\bigcirc$ ; argon,  $\bigtriangledown$ ; nitric oxide,  $\diamondsuit$ ; oxygen,  $\bigcirc$ .

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#### EFFECT OF ADDED GASES

Addition of nitrogen or argon (133 mbar) reduced the rates of formation of the gaseous products by about 90 %. Fig. 3 shows the effect for the ethylene formed from *ets.* Above 130 mbar the reduced yield was constant. Addition of oxygen or nitric oxide (fig. 3) reduced the yield of ethylene in the same way as nitrogen or argon. The ethane yield was reduced to a smaller constant value but the yields of propane and butane were reduced to zero. Similar results were obtained with *pts*: the rates of formation were reduced by 92 % if 66 mbar of nitrogen was added and then they remained constant up to 800 mbar. Oxygen removed all the butane but there were residual reactions forming ethane and propylene at high pressures of oxygen.

## EFFECT OF TEMPERATURE

Results of experiments with *ets* at various temperatures are shown in fig. 4. The rate of methane formation increased continuously up to 150°C while the rates for propane and butane were reduced. The ethylene rate remained nearly constant and the ethane rate showed a mixed behaviour.



FIG. 4.—Variation of product yield with temperature in the photolysis of *ets.* p(ets) = 13 mbar; methane,  $\triangle$ ; ethane,  $\bigcirc$ ; ethylene,  $\diamondsuit$ ; propane,  $\bigtriangledown$ ; butane,  $\bigcirc$ .

#### DISCUSSION

### ets: MOLECULAR PRIMARY REACTIONS

Added nitrogen and oxygen reduce the yield of ethylene by the same amount so that it is probably a molecular product. Small fractions of the ethane and methane are formed by molecular elimination too. The major molecular elimination reaction is

$$C_2H_5$$
)Sn(CH<sub>3</sub>)<sub>3</sub> +  $hv(\lambda = 185 \text{ nm}) \rightarrow C_2H_4$ ;  $\phi(1) = 0.40$  (1)

The quantum yield is calculated by extrapolating the ethylene yield to zero pressure.

#### ets: RADICAL PRIMARY REACTIONS

The main primary reaction is a split into free radicals as shown by the nature of the products and the reduction of their yields by added oxygen. Since there is a rough equivalence between the yields of the products formed from methyl radicals,  $CH_4$ ,  $C_2H_6$  and  $C_3H_8$ , and those from ethyl radicals,  $C_3H_8$  and  $C_4H_{10}$ , it is likely that an ethyl radical is detached in the primary act together with one or two methyl radicals.

There are two main possibilities :

$$C_{2}H_{5}Sn(CH_{3})_{3} + hv(\lambda = 185 \text{ nm})$$
  

$$\rightarrow C_{2}H_{5} + CH_{3} + Sn(CH_{3})_{2}; \quad \phi(2) \sim 0.55, \qquad (2)$$
  

$$\rightarrow C_{2}H_{5} + 2CH_{2} + SnCH_{3} \qquad (3)$$

With tetramethylstannane the reaction equivalent to (3) was the principal process because of the formation of metallic tin.<sup>1</sup> Here only polymer is formed and this, together with the equivalence between the products from methyl and ethyl radicals, indicates that reaction (2) is the main process.

For total primary quantum yield to be one,  $\phi(2)$  would be ~0.55 since  $\phi(1) = 0.40$ . When the quantum yields of the products are summed the quantum yields for the formation of methyl and ethyl radicals are greater than 1;  $\phi(CH_3) \sim 1.5$  and  $\phi(C_2H_5)$  $\sim$ 1.6. There are two possible explanations for the discrepancy. Either radical abstraction reactions such as

$$CH_3 + C_2H_5Sn(CH_3)_3 \rightarrow C_3H_8 + Sn(CH_3)_3$$
(4)

occur or there is a reaction between the excited state and the reactant which decomposes both molecules gaining the necessary energy from the formation of a ditin compound or a hydrocarbon molecule. The plot in fig. 1 was intended to eliminate these possibilities by enabling an extrapolation to zero pressure of reactant to be made; if these reactions are important at very low pressures then the extrapolation is invalid. It is evident that the sum of the quantum yields of principal primary reactions, (1) and (2), is close to one at zero pressure.

# ets: SECONDARY REACTIONS

The products ethane, propane and butane are formed by

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{5}$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \tag{6}$$

$$C_2H_5 + C_2H_5 \to C_4H_{10}.$$
 (7)

The ratio,  $\gamma = R(C_3H_8)/[R(C_2H_6)R(C_4H_{10})]^{\frac{1}{2}}$ , where  $R(C_2H_6)$  is the rate of formation of ethane, should be equal to the cross combination ratio,  $k_6/(k_5k_7)^{\frac{1}{2}}$  which is  $^{4}$  2.0. The value found is 2.3. The difference is probably due to the abstraction reaction (4) contributing to the propane yield and being slightly more favourable than the corresponding reactions which form butane and ethane. Both this ratio and the primary reaction (2) indicate that the  $Sn-C_2H_5$  bond can be broken more readily than the Sn-CH<sub>3</sub> bond.

At the low pressures used methane will be formed by disproportionation :

$$CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4 \tag{8}$$

The ratio  $R(CH_4)/R(C_3H_8)$  corrected for the methane formed molecularly is 0.044 in agreement with the previous value <sup>4</sup> for  $k_8/k_6$ . It is not possible to detect the disproportionation reaction corresponding to (6) due to the molecular ethylene present and the low value of the disproportionation/recombination ratio.<sup>4</sup>

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#### At higher temperatures, fig. 4, hydrogen abstraction augments the methane yield;

$$CH_3 + C_2H_5Sn(CH_3)_3 \rightarrow CH_4 + C_2H_5Sn(CH_3)_2CH_2.$$
(9)

The uncertainty about the primary reaction removes any confidence in our estimates of  $k_9$  but a good Arrhenius plot gave an approximate value for the activation energy,  $E_9 = 46 \text{ kJ mol}^{-1}$ . The value is higher than the equivalent value found for tetramethylstannane.<sup>1</sup>

The decreased yields of the other products at high temperatures points to the consumption of the radicals in hydrogen abstraction reactions (9) and in recombination with the increased number of alkyl tin radicals available from reactions such as (9). The ratio  $\gamma$  approaches 2.0 as the temperature is raised showing that products are formed in recombination reactions and that the relative importance of the radical abstraction reactions such as (4) decreases. This is consistent with the results from tetramethylstannane where abstraction of a methyl radical was shown to have only a small temperature coefficient compared to abstraction of hydrogen.

#### PHOTOLYSIS OF pts

The results are similar to those from *ets* and have been analyzed in the same way. Addition of oxygen did not completely supress the yield of any gaseous product and comparison of results with added nitrogen suggests that some methane (60 %) ethylene (100 %) ethane (5 %) propylene (75 %) and butane (5 %) are formed molecularly. The most important molecular reactions are :

$$C_{3}H_{7}Sn(CH_{3})_{3} + hv(\lambda = 185 \text{ nm})$$
  
 $\rightarrow C_{3}H_{6}; \quad \phi(10) \sim 0.24; \quad (10)$ 

$$\rightarrow C_2 H_4; \phi(11) \sim 0.07.$$
 (11)

At this wavelength the number of molecular primary reactions increases as the homologous series is ascended. A similar effect is observed with the olefins.<sup>5</sup>

The ratio of 2 : 1 found from the product yields for the fragments from methyl and propyl radicals favours a primary split into a propyl and two methyl radicals as was found for tetramethyl-stannane :

$$C_{3}H_{7}Sn(CH_{3})_{3} + h\nu(\lambda = 185 \text{ nm})$$
  

$$\rightarrow C_{3}H_{7} + 2CH_{3} + Sn(CH_{3}). \qquad (12)$$

As before the total primary quantum yield appears to be above one probably due to abstraction reactions and the products found are formed either by abstraction or recombination.

#### QUENCHING REACTION (ets, pts)

For both compounds the yields of products could be reduced to 10 % of their usual values by adding 130 mbar of either nitrogen or argon, fig. 3. The residual reaction was independent of pressure. For the molecular products oxygen had a similar effect. The uniform decrease for all products suggests that an excited state precursor is being deactivated :

$$s + hv \rightarrow s^*$$
 (13)

$$s^* \rightarrow \text{products}$$
 (14)

$$s^* \rightarrow s^{**}$$
 (15)

$$s^{**} \rightarrow \text{products}$$
 (16)

$$s^{**} + \mathbf{M} \to s + \mathbf{M}. \tag{17}$$

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Here s is the stannane,  $s^*$  an unquenchable excited state,  $s^{**}$  the quenchable state, and M is argon, nitrogen or oxygen. With the usual steady-state treatment the rate  $R_p(p)$  of formation of a product at pressure, p, of added gas, can be related to the concentration of M by  $[R(p) - R(\infty)]^{-1} = ((k_{14} + k_{15})/k_{15}I\phi)(1 + k_{17}[M]/k_{16})$ , where I is the incident light intensity and  $\phi$  the quantum efficiency of (13). As fig. 5 shows, linear plots are obtained for each of the products from which the intercept/slope ratios give  $k_{17}/k_{16}$  to be  $1.35 \times 10^{-3}$  mol l.<sup>-1</sup> (ets) and  $1.20 \times 10^{-3}$  mol l.<sup>-1</sup> (pts). If collision quenching occurred on each collision the lifetime of s\*\* in each case would be  $\sim 10^{-8}$  s.



FIG. 5.—A plot of  $[R(p)-R(\infty)]^{-1}$  against pressure of added nitrogen in the photolysis of ets for the yields of ethylene,  $\triangle$ ; ethane,  $\bigcirc$ ; propane,  $\bigtriangledown$ .

It is evident that the alkylstannanes like the olefins have an excited state which is a precursor for decomposition and which can be deactivated easily by collision with simple molecules. Unlike the olefins the reactant itself cannot act as a quencher and there is certain fraction of the reaction which proceeds through an unquenchable state. The nature of  $s^*$  and  $s^{**}$  is not known.  $s^*$  is probably a singlet state formed on absorption of light while s\*\* could be either the triplet state or the ground state vibrationally excited to make it isoenergetic with s\*.

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