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FLASH PHOTOLYSIS OF TETRAETHYLTIN AND TETRAVINYLTIN

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Summary

A study is presented of the gas phase flash photolytic decomposition of tetravinyl- and tetraethyl-tin, both in the pure state and diluted with argon, oxygen and sulphur hexafluoride. These organotin compounds decompose by molecular or radical elimination with approximately equal probability. The radicals produced are vibrationally excited and undergo various reactions depending on the extent of their excitation. The major hydrocarbon products are those containing two carbon atoms i.e. ethane, ethylene and acetylene; 1,3-butadiene and n-butane are also significant products.

An estimate of the recombination to disproportionation rate constant ratio for vinyl radicals was obtained, viz. k_r/k_d 0.27.

Introduction

During the course of an investigation of the applicability of various organometallic compounds as sources of simple alkyl and alkene radicals in flash photolysed systems we have obtained some very interesting results from tetraethyl- and tetravinyl-tin (TET and TVT respectively). These results are reported herein and provide information on the photodecomposition of *(a)* organotin species and *(b)* organometallics obtaining C_2-units.

Few previous studies of the photodecomposition of simple organotin compounds have been reported in the literature. Borrell and Platt [1] showed that the continuous photolysis of tetramethyltin at 185 nm produced primarily radical elimination whereas in a similar study of ethyltrimethyltin [2] molecular elimination of ethylene was almost as important as radical elimination. The only previous flash photolysis study of an organotin compound is that of tetramethyltin [3]. The high yield of unsaturated hydrocarbons obtained in this system was considered to be due to reactions of vibrationally excited methyl radicals produced in the initial photodecomposition.

Experimental

The flash photolysis experiments were conducted in the apparatus shown schematically in Fig. 1. Details of the quartz lamp and the conventional discharge circuitry have been given elsewhere [4]. All experiments described herein were initiated by discharging 1066 J through the lamp, the flash profile width at 1/e peak height being 30 μs. Uranyl oxalate actionometry showed that the lamp emitted 5.79 ± 0.11 $\times 10^{18}$ quanta per flash in the wavelength range 195-490 nm. Evidence has been presented elsewhere that the intensity of this emitted light was sensibly constant over this wavelength range [3,5].

The reaction vessel body was constructed from 33.0 mm O.D. pyrex whilst the inner thimble was of 20 mm I.D. vitreosil quartz. The volume (25 ml nominal) of each of the several vessels used was calibrated so that the amounts of reactants and products could be accurately determined for each experiment. Subsequent to the photolysis, a known amount of internal standard was introduced from an external gas handling system of calibrated volume; the reaction vessel was then raised to atmospheric pressure by the addition of dry nitrogen. After sufficient time had been allowed for complete mixing, samples were removed via the septum plug for gas chromatographic analysis.

Gas chromatography

Gas chromatographic analyses were performed on a Perkin—Elmer 880 Gas Chromatograph equipped with flame ionisation detection and a Kent Chromalog Peak Integrator. The hydrocarbon products were separated on matched 2m (4 mm O.D.) stainless steel columns packed with Squalane—Alumina H (3/97). Nitrogen, flow rate 0.5 ml s^{-1}, was used as carrier gas and the columns were operated in the 40-100°C region. The products were identified by comparing their retention times with those of pure hydrocarbons and synthetic mixtures of known composition; identifications were confirmed by also performing the comparisons on silica gel columns. Quantitative data were obtained by calibration of the gas chromatographic response to each hydrocarbon with reference to *cis*-2-butene which was found to be the most suitable internal standard.

UV spectra

A pair of optically matched 1 cm 'Spectrosil' cells were used in conjunction with a Pye Unicam SP1800 ultraviolet spectrometer to obtain the adsorp-

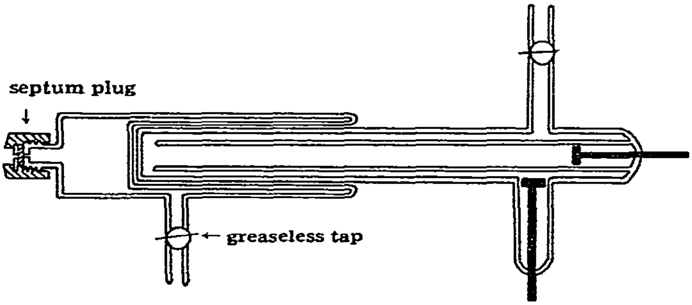
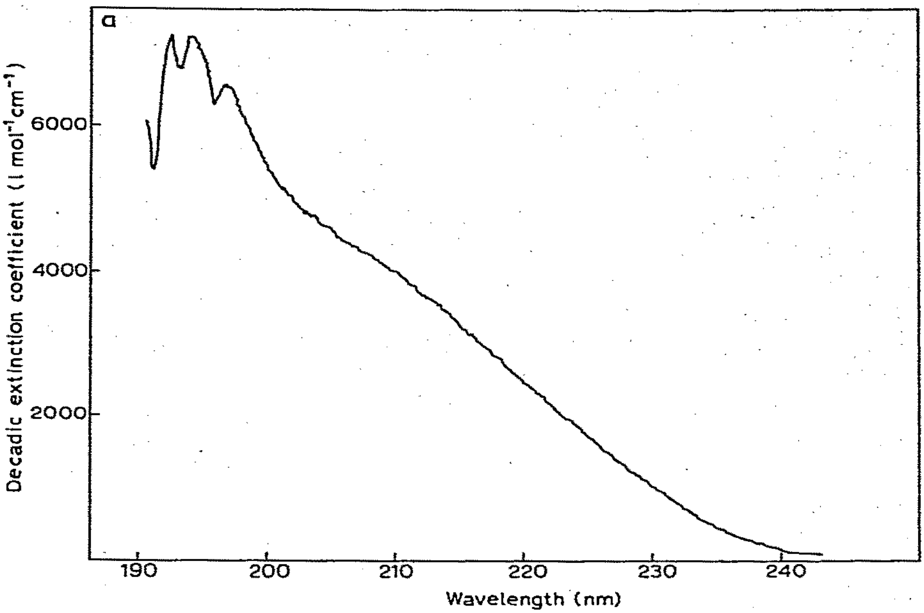


Fig. 1. Flash photolysis lamp and cell configuration.



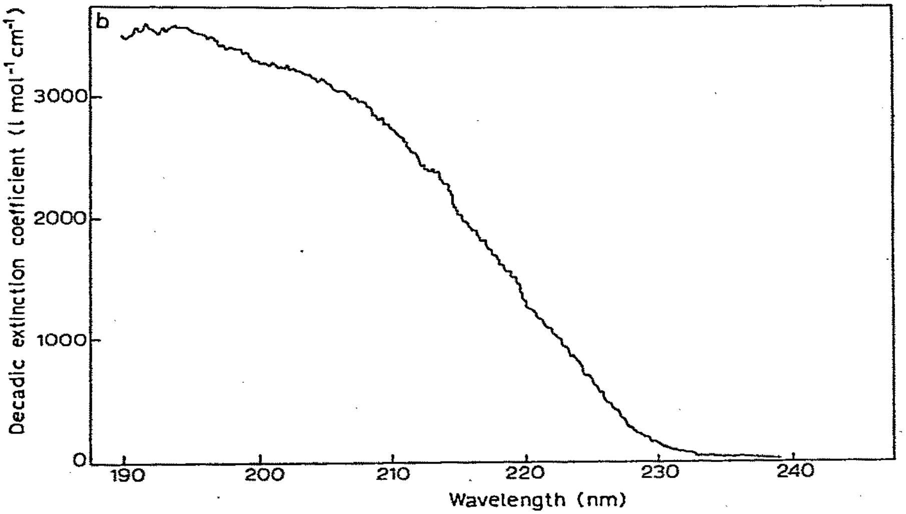


Fig. 2a. Ultraviolet absorption spectrum of TVT.

Fig. 2b. Ultraviolet absorption spectrum of TET.

tion spectra of TET and TVT. These spectra, which are not available in the literature, are presented in Fig. 2.

Materials

TET (99% purity) was obtained from Ventron, Alfa Products and TVT (98% purity) from Koch—Light Laboratories. Both compounds were outgassed by freeze—thaw cycles 'in vacuo', but were not further purified before use. Calibration gases and sulphur hexafluoride were obtained from either E.D.T. Supplies Ltd. or Matheson Ltd. High Purity argon and oxygen were supplied by BOC Ltd.

Results

Tetraethyltin

The flash photolysis of pure TET in the pressure range 60-145 Nm^{-2} (0.47-1.09 Torr) yielded ethylene (54% of total detected products), hydrogen (18%), ethane (17%), n-butane (6%) and propane (4%); the hydrogen being an estimate based on mass deficit. Acetylene, propene and methane were detected as minor products amounting to about 1% of the total. The relative yields of the products were independent of the amount of TET decomposed. Neither polymeric material nor metallic tin deposits were observed. The influence of excited species on the reaction mechanism was investigated by studying the effect of dilution, of an approximately constant pressure of TET (65 Nm^{-2} nominal), by the inert colliders argon and sulphur hexafluoride. Radical effects were also investigated using the scavenger oxygen. Fig. 3 shows the variation of yield (hereafter yield refers to actual product yield normalised to the initial organometallic pressure) with dilution ratio '*D*' (pressure of diluent ÷ initial organometallic pressure) for the products ethylene, ethane, n-butane, propane and hydrogen. Increasing the amount of all three diluents reduces the product yields to limiting values, the average limiting values for the major products are given in Table 1. For ethylene these limiting values decrease in the order argon, oxygen and sulphur hexafluoride. Similar behaviour is observed in the case of ethane except that the limiting yield in argon is appreciably greater than in oxygen or sulphur hexafluoride. The n-butane yield is independent of the extent of argon dilution while the

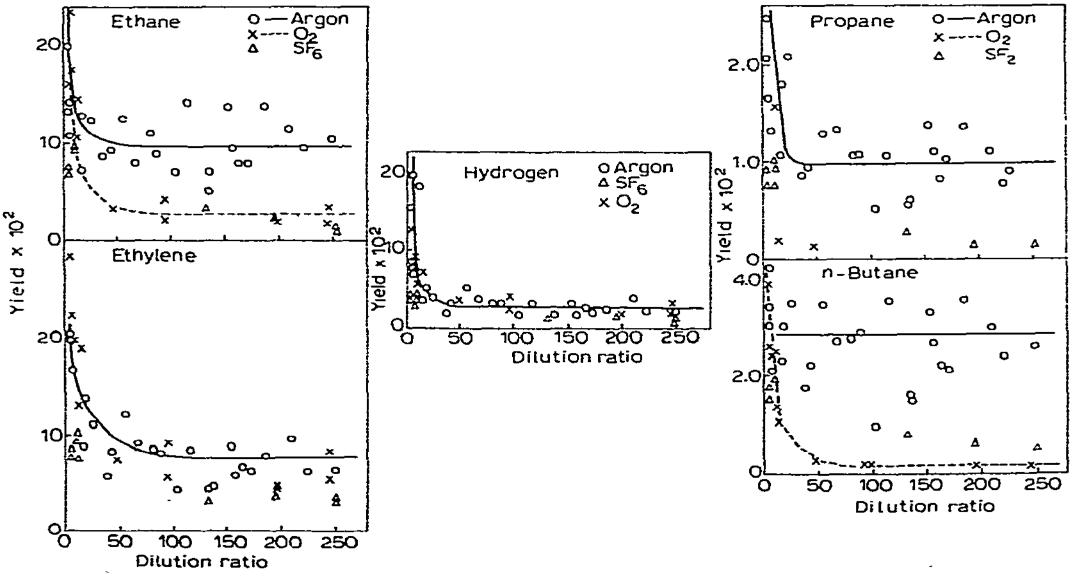


Fig. 3. Plots of yield vs. dilution ratio for products from TET with various diluents.

TABLE 1

AVERAGE LIMITING YIELDS AND PERCENTAGE DECOMPOSITIONS FOR MAJOR PRODUCTS FROM TET

Diluent	Limiting product yields (X 10^2)			Percent decomposition[a]
	C_2H_4	C_2H_6	n-C_4H_{10}	
Argon	7.49	0.96	2.82	7.48
Oxygen	6.18	0.23	0.15	3.46
SF_6	3.18	0.10	0.50	2.46

[a] 8.5% of the TET molecules are estimated to have absorbed light [Appendix (a)].

other diluents markedly reduce this yield; the limiting yield is lower in the presence of oxygen. The propane yield decreases on the addition of all three diluents; the limiting yield in the case of argon is 1.0 X 10^{-2}, in the case of sulphur hexafluoride 10^{-3}, both limits being reached at about *D* 25. No propane is detected in the presence of oxygen above *D* 50. All three diluents reduced the estimated hydrogen yield to a limiting value of ca. 10^{-2} at *D* 50.

Fig. 4 shows the effects of argon and oxygen on the yield of ethylene and

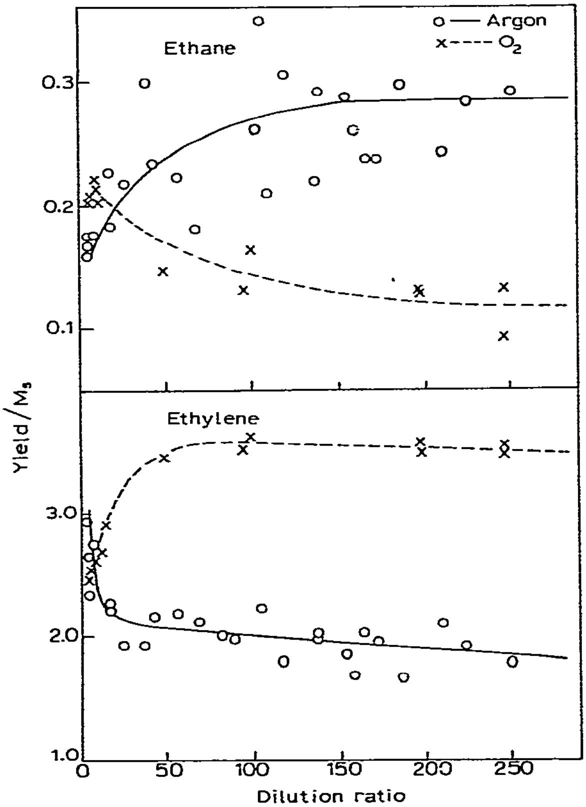


Fig. 4. Plots of yield normalised by M_s vs. dilution ratio for major products from TET with various diluents.

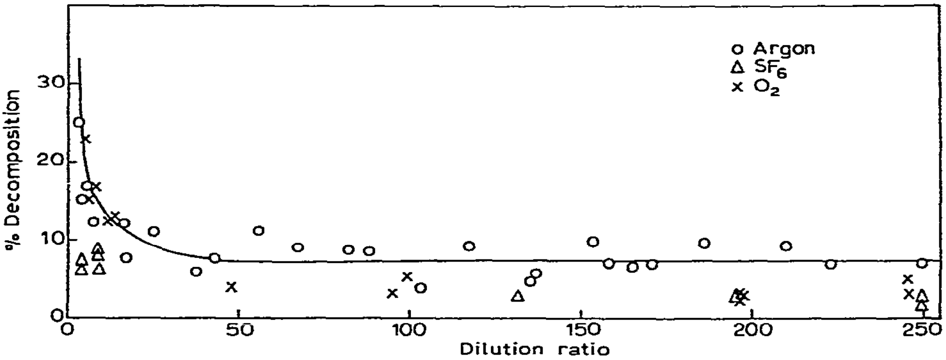


Fig. 5. Plots of percentage decomposition vs. dilution ratio from TET with various diluents.

ethane relative to a quantity M_s which was defined as total carbon in detected products divided by number of carbon atoms in the parent molecule, i.e. 8 for TET. Oxygen markedly increases the relative yield of ethylene whereas argon decreases it. This behaviour was mirrored by the relative yield of hydrogen whereas it was reversed for ethane (Fig. 4) and n-butane. The relative propane yield was essentially independent of the extent of argon dilution whereas in oxygen it was reduced to zero above D 50.

In the later discussion of the primary processes occurring in the TET system, we interpret our data as indicating that two C_2 units are formed per substrate molecule decomposed. On this basis, the amount of TET decomposed expressed as a percentage of initial TET is plotted against dilution ratio in Fig. 5. This percentage decomposition is seen to decrease with increasing dilution ratio, the average limiting value being 7.48% in argon, 3.46% in oxygen and 2.46% in sulphur hexafluoride (Table 1).

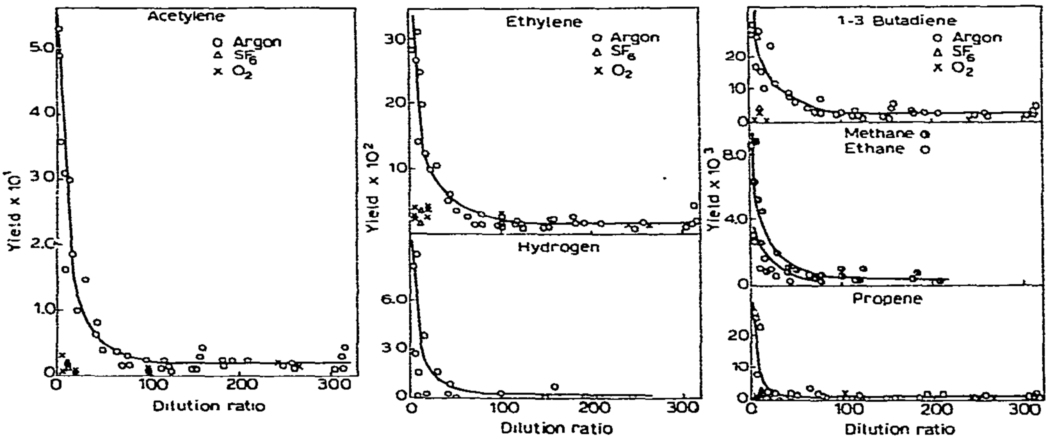


Fig. 6. Plots of yield vs. dilution ratio for products from TVT with various diluents.

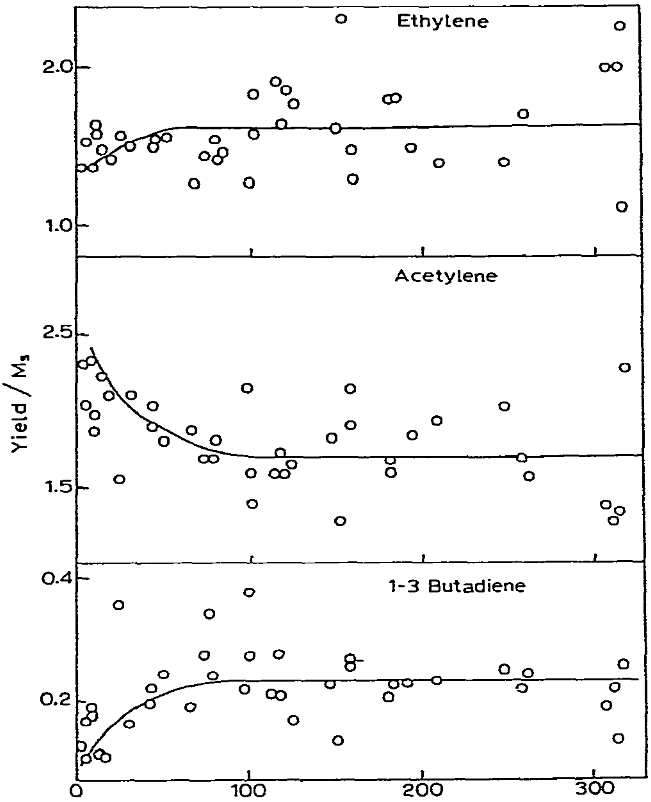


Fig. 7. Plots of yield normalised by M_S vs. dilution ratio for major products from TVT with various diluents.

Tetravinyltin

The flash photolysis of pure TVT in the pressure range 65-330 Nm^{-2} (0.5-2.5 Torr) produced acetylene (52%), ethylene (36%), hydrogen (estimated 8%), and 1,3 butadiene (3%). The minor products detected were methane, propane and ethâne, these accounted for about 1% of the total products. In addition trace quantities of 1-butene, polymer and metallic tin deposits were observed. The relative yields of the products were shown to be independent of the amount of TVT decomposed and the energy discharged through the flash lamp. The influence of any excited species or free radicals was investigated by studying the

TABLE 2

AVERAGE LIMITING YIELDS AND PERCENTAGE DECOMPOSITIONS FOR MAJOR PRODUCTS FROM TVT

Diluent	Limiting product yields (X 10^2)			Percent decomposition[a]
	C_2H_2	C_2H_4	1,3-C_4H_6	
Argon/SF_6	1.73	1.65	0.22	2.02
Oxygen	1.05	1.01	0.05	1.48

[a] 11.25% of the TVT molecules are estimated to have absorbed light.

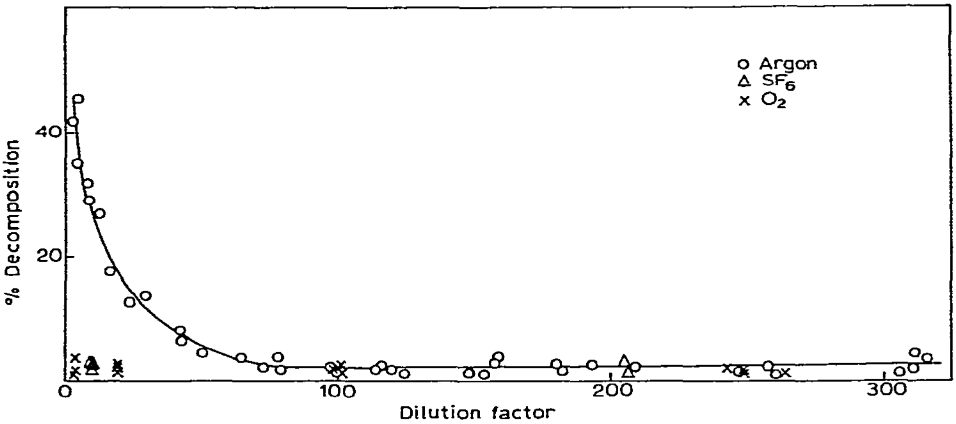


Fig. 8. Plot of percentage decomposition vs. dilution ratio from TVT with various diluents.

effect of the same diluents as were used in the TET case on an approximately constant pressure (200 Nm^{-2} nominal) of TVT. Fig. 6 shows the variation of product yields with increasing dilution ratio. Argon reduced the yield of acetylene to an average limiting value of about 10^{-2} above D 100; oxygen and sulphur hexafluoride very significantly reduced the yield, even at low dilutions, to a similar limit. Similar behaviour was observed in the case of the other products but it should be noted that oxygen decreased the 1,3-butadiene yield to a greater extent than it did the yield of ethylene and acetylene. The average limiting high dilution results for the major products are given in Table 2.

The variations in the major product yields, relative to the quantity M_s, with argon dilution are shown in Fig. 7, the relative yield of acetylene is seen to decrease eventually levelling off above D 100; this is mirrored by an increase in the relative yields of ethylene and 1,3-butadiene below D 100. Fig. 8 shows the effect of increasing dilution on the percentage decomposition (calculated assuming two C_2 units are formed per TVT molecule photodecomposed). Oxygen and sulphur hexafluoride reduce the percentage decomposition to a limiting value, 2.02% and 1.48% respectively, at very low dilutions whereas argon produces a much more gradual reduction to an average of 2.02% at about D 100, Table 2.

Discussion

Tetraethyltin

Primary processes. An accurate estimation of the extent of light absorption in our experiments cannot be obtained using the Beer—Lambert law because this does not take into account depletion of the absorber resulting from the relatively high extinction coefficient of TET. This estimate has, therefore, been obtained using an analytical formula previously developed for such conditions [5]. The formula is

$$\frac{M_t}{M_0} = \frac{1}{\epsilon M_0}\{\ln[(\exp(\bar{\epsilon} M_0 - 1)\exp(-\alpha \bar{\epsilon} M_0)) + 1]\}$$

where M_0 and M_t are the initial and final number of moles of TET in the light path per unit area (mol cm^{-2}), $\bar{\epsilon}$ the mean Napierian extinction coefficient (5.08×10^3 l mol^{-1} cm^{-1}) over the λ-range absorbed and $\alpha = n_Q/M_0$ where n_Q is the incident number of quanta per unit area in the absorption wavelength region of TET divided by Avogadro's number. Using the cell division discussed in Appendix (a) it was estimated that 8.5% of the TET molecules absorb light.

The light absorbed by the TET has insufficient energy (630-510 kJ mol^{-1}) to cause complete dissociation giving four C-units (mean Sn—C bond strength in tetramethyltin [1] is about 200 kJ mol^{-1}). We have, therefore, worked on the assumption that two C_2-units are lost per TET molecule decomposed and calculated the percentage TET decomposed from the total carbon content in the detected products. The results of these calculations using data obtained under limiting conditions of high dilution are given in Table 1. The agreement between the figure obtained in argon and the estimated % TET absorbing light supports the proposal that two C_2-units are lost per TET molecule photodecomposed.

The most probable primary processes resulting in the loss of two C_2-units per molecule photodecomposed are:

$$Sn(C_2H_5)_4 + h\nu \rightarrow Sn(C_2H_5)_4^* \rightarrow Sn(C_2H_5)_2H_2 + 2\,C_2H_4 \qquad \Delta U_{298} \quad 106 \text{ kJ mol}^{-1} \quad (1)$$

$$Sn(C_2H_5)_4 + h\nu \rightarrow Sn(C_2H_5)_4^* \rightarrow Sn(C_2H_5)_2 + C_2H_6 + C_2H_4 \qquad \Delta U_{298} \quad -10 \text{ kJ mol}^{-1} \quad (2)$$

$$Sn(C_2H_5)_4 + h\nu \rightarrow Sn(C_2H_5)_4^* \rightarrow Sn(C_2H_5)_2 + C_4H_{10} \qquad \Delta U_{298} \quad -101 \text{ kJ mol}^{-1} \quad (3)$$

$$Sn(C_2H_5)_4 + h\nu \rightarrow Sn(C_2H_5)_4^* \rightarrow Sn(C_2H_5)_2 + 2\,C_2H_5^{\cdot} \qquad \Delta U_{298} \quad 239 \text{ kJ mol}^{-1} \quad (4)$$

The changes in internal energies were estimated using the empirical method of Benson [6], they show that all these reactions are energetically feasible since the input of light energy is in the range 630-510 kJ mol^{-1}. From the figures given in Table 1, it can be estimated that about 52% of the C_2-units appearing in the final products obtained in argon derive from radical reactions, thus reaction 4 is an important primary process. The oxygen experiments show that about 83% of the ethylene, which accounts for 61% and 82% of all products in argon and sulphur hexafluoride respectively, is produced via molecular elimination in argon. The same experiments indicate that very little ethane is derived from such a route, thus reaction 1 must be by far the most significant molecular elimination process. Only about 5% of the detected butane was produced via molecular elimination thus reaction 3 is insignificant. Overall, molecular elimination accounts for about 48% of products in argon.

The effect of sulphur hexafluoride on the product yields is very significant. Under conditions of high dilution the yields are about one third of those obtained under identical conditions in argon. If the fall in yields on dilution were due to deactivation of the same excited species then the limiting yield in argon would be expected to be approximately the same as that in sulphur hexafluoride, this limit being reached at a higher dilution ratio. This is not the case. We suggest that a possible explanation for this effect is that absorption of light can produce two electronically excited states of TET, one can be quenched by sulphur hexafluoride only whereas the second state can be quenched by neither sulphur hexafluoride nor argon. Borrell and Platt [1,2], in a study of the static photolysis of ethyltrimethyltin and tetramethyltin, have suggested the formation of two photo-excited states of the parent species. One state was considered to be quenchable and the other not. Since the yields in oxygen are between those in argon and sulphur hexafluoride it is possible to postulate, considering the study of Dingledy and Calvert [7], that oxygen·does not deactivate either excited parent species.

The addition of oxygen causes a marked reduction of the yield of all products except ethylene. The study of the reaction between ethyl radicals and oxygen by Dingleby and Calvert [7] indicated that very little ethylene is produced in this system. Therefore, the yield of ethylene which we detected in the presence of oxygen must result from molecular elimination and the products whose yields are markedly effected by the presence of oxygen must derive from radical reactions presumably initiated via reaction 4. The products propane, propene and methane strongly indicate the presence of methyl radicals in the reaction sequence leading to their formation. These minor products were not detected on dilution with all three diluents. The exception was propane which, in argon and sulphur hexafluoride decreased rapidly to a constant yield on increasing dilution. These observations suggest that the methyl radicals result from dissociation of excited ethyl radicals (see below).

Reactions at very low dilution. On decreasing the dilution by all the diluents, the yields of all the products rise markedly from their limiting high dilution values. Estimation of the amount of TET decomposed, based on the proposal that two C_2-units are produced per TET molecule photodissociated, from the carbon content of the detected products shows that in the low dilution region the number of TET molecules decomposed is approximately twice the number estimated to absorb light, Fig. 5. These observations can only result from pyrolysis of the TET due to adiabatic heating and/or attack by excited ethyl radicals on the substrate molecules causing further decomposition above that accounted for by light absorption. The adiabatic temperature rise was estimated to be ca. 180°C using the equation proposed by Meyer [8]. No direct measurement of the rate constant for the pyrolysis of TET is available in the literature but that for the pyrolysis of diethylmercury [9] is 2×10^{-7} s^{-1} at 180°C. If the rate constant for pyrolysis of TET is similar, then the adiabatic temperature rise cannot account for the increased decomposition of TET above that absorbing light, observed at low dilution. It appears, therefore, that the increase observed is due to attack on the parent by excited ethyl radicals.

The presence of excited ethyl radicals in flash photolysis systems has been suggested in several previous studies. Their presence in our experiments is indicated by the rapid rise in the ethylene yield curve (Fig. 3) on decreasing dilution which is probably due to the well known decomposition of ethyl radicals to yield ethylene and a hydrogen atom.

If excited ethyl radicals are attacking the parent molecules and resulting in enhanced decomposition, then collision theory can be invoked to estimate the dilution at which this effect will be negligible. The method is presented in Appendix b, and in the case of TET, the appropriate dilution ratio is calculated as 60 which is in fair agreement with the observations, shown in Fig. 3, that the yields of the major products start to rise, with decreasing dilution, in the dilution ratio range 45-65. The percentage decomposition also increases in this region, Fig. 5. This evidence supports the suggestion that there is attack on the substrate molecules by excited ethyl radicals when TET is flash photolysed either in the pure state or under low dilution conditions. This attack will presumably be via reactions of the type:

$$C_2H_5^\dagger + Sn(C_2H_5)_4 \rightarrow C_2H_6 + Sn(C_2H_5)_2C_2H_4 \tag{6}$$

$$C_2H_5^\dagger + Sn(C_2H_5)_4 \rightarrow C_4H_{10} + Sn(C_2H_5)_3 \tag{7}$$

Radical reactions. No acetylene or propene and very little ethane, n-butane and propane were detected after the TET had been flashed photolysed in the presence of oxygen. For ethylene and hydrogen the decrease in yield on dilution with oxygen almost matches that in argon. Thus the production of ethyl radicals (reaction 4) must be a major primary process and the species whose yields are very sensitive to the presence of oxygen must result from a radical mechanism initiated by ethyl radicals. The combination and disproportionation reactions of the ethyl radicals would produce n-butane, ethylene and ethane via:

$$C_2H_5^\bullet + C_2H_5^\bullet \xrightarrow{+M} n\text{-}C_4H_{10} \tag{8}$$

$$C_2H_5^\bullet + C_2H_5^\bullet \longrightarrow C_2H_4 + C_2H_6 \tag{9}$$

As previously mentioned, the products propane, propene and methane indicate that methyl radicals were produced, under these conditions, probably via a mechanism involving exited ethyl radicals.

$$C_2H_5^{\bullet\dagger} \rightarrow C_2H_4 + H^\bullet \tag{10}$$

$$C_2H_5^\bullet + H^\bullet \rightarrow C_2H_6^\dagger \begin{cases} \xrightarrow{+M} C_2H_6 \\ \rightarrow 2CH_3^\bullet \end{cases} \tag{11}$$

$$C_2H_5^\bullet + CH_3^\bullet \begin{cases} \rightarrow C_2H_6 + CH_4 \\ \rightarrow C_3H_8^\dagger \begin{cases} \xrightarrow{+M} C_3H_8 \\ \rightarrow C_3H_6 + H_2 \end{cases} \end{cases} \tag{12}$$

$$C_2H_5^{\bullet\dagger} + C_2H_5^{\bullet\dagger} \rightarrow C_2H_6 + C_2H_4^\dagger \tag{13}$$

$$C_2H_4^\dagger \rightarrow C_2H_2 + H_2 \tag{14}$$

Tetravinyltin

Primary processes. Estimation of the amount of light absorption was made using the analytical formula discussed in the case of TET. The data specific to the TVT experiments can be summarised: $\bar{\epsilon} = 6.56 \times 10^3$ l mol^{-1} cm^{-1} between 195-240 nm the wavelength range of absorption by TVT, the initial concentration of TVT was 1×10^{-6} mol dm^{-3}. We estimate that 11.25% of the TVT molecules absorb light. Table 2 gives a comparison of this figure with the percentage decomposition calculated, on the assumption that two C_2-units are produced per substrate molecule photodecomposed, from the experimental product yields at high dilution. The latter assumption is based on previous studies of the photodecomposition of TET (this paper), dimethylmercury [10] and tetramethyllead [3].

The detected decomposition, at high dilution, is well below the estimated extent of light absorption. Thus a quenching process must be occurring and since there is a residual yield, an unquenchable species must be present. Argon and sulphur hexafluoride give the same percentage decomposition at high dilution whereas that in presence of the radical scavenger oxygen is slightly lower. This suggests the production of two photoexcited states, one which can be quenched by all three diluents and the other by none. That oxygen has a greater effect, than argon and sulphur hexafluoride on the limiting yield at high dilution indicates that radical reactions as well as molecular elimination reactions result from the decomposition of the excited TVT molecules. The most likely primary decompositions are:

$$Sn(C_2H_3)_4 \overset{h\nu}{\rightarrow} Sn(C_2H_3)_4^* \rightarrow Sn(C_2H_3)_2 + C_2H_2 + C_2H_4 \quad \Delta U_{298}\ 73\ \text{kJ mol}^{-1} \qquad (15)$$

$$Sn(C_2H_3)_4 \overset{h\nu}{\rightarrow} Sn(C_2H_3)_4^* \rightarrow Sn(C_2H_3)_2 + C_4H_6 \quad \Delta U_{298}\ -95\ \text{kJ mol}^{-1} \qquad (16)$$

$$Sn(C_2H_3)_4 \overset{h\nu}{\rightarrow} Sn(C_2H_3)_4^* \rightarrow Sn(C_2H_3)_2 + 2\ C_2H_3^{\bullet} \quad \Delta U_{298}\ 369\ \text{kJ mol}^{-1} \qquad (17)$$

The changes in internal energies were estimated using Benson [6] 'Additivity Rules', they show that all these reactions are energetically possible since the average energy of the photons absorbed is 556 kJ mol^{-1}. The residual yields in the oxygen experiments indicate that about 56% of the hydrocarbons detected at high dilution are produced via molecular elimination. Reaction 15, therefore, appears to be the major primary decomposition process. Radical elimination, i.e. reaction 17, is also very significant since about 43% of the detected products derive from radical reactions at high dilution. Little 1,3-butadiene was detected in the high dilution oxygen experiments, reaction 16 is, therefore, unimportant.

Reactions at very low dilution. As was the case in the TET experiments, all product yields were very much greater in low dilution compared to the high dilution experiments. In the former region the percentage TVT decomposing to hydrocarbons is greater than the percentage of TVT molecules estimated to absorb light, Fig. 8. The adiabatic temperature rise in this region is not more than 100 K. No rate data for TVT pyrolysis is available, but data for the pyrolysis of divinylmercury [11] can be extrapolated to give a rate constant of 10^{-16} s^{-1} at 373 K. If the rate constant for the TVT pyrolysis is similar, then adiabatic heating cannot account for the observed enhanced decomposition at low dilution. This enhancement must be due to attack on the parent by excited vinyl radicals. The presence of such radicals is indicated by the increasing acetylene/ethylene ratio with decreasing dilution.

If the yields are due to an excited radical attacking a parent molecule, the dilution at which they become constant can be estimated by the method described in Appendix b; the values of the various parameters relevant to TVT are: a 0.319, x 63.8 and y 9.6. Using the data in Table 4, the leveling off point is estimated to occur at D 107 which agrees well with the observation (Figs. 6 and 8) that the yields became constant in the dilution ratio range 90-110. This supports the postulate that excited vinyl radicals cause the enhanced decomposition at low dilution. These radicals probably abstract either a hydrogen atom or radical group from the parent molecule to produce a stable hydrocarbon and an unstable tin species which can undergo subsequent decomposition, e.g.

$$C_2H_3^{\cdot\dagger} + Sn(C_2H_3)_4 \rightarrow Sn(C_2H_3)_3 + C_4H_6 \qquad (18)$$

$$C_2H_3^{\cdot\dagger} + Sn(C_2H_3)_4 \rightarrow Sn(C_2H_3)_3C_2H_2 + C_2H_4 \qquad (19)$$

A reaction equivalent to 18 was considered to be important in the continuous photolysis of divinylmercury [12] but distinguishing between these two reactions is not possible with the present data.

Radical reactions. The observations that oxygen reduces the yield of the major products acetylene and ethylene and that the other products are not detected at high oxygen dilutions indicates that vinyl radicals must be produced in a major primary process, reaction 17, and that the affected products derive from a radical mechanism initiated by these vinyl radicals. The major radical reactions are combination and disproportionation to give 1,3-butadiene, acetylene and ethylene respectively. The excess of acetylene over ethylene observed at low dilutions is presumably due to dissociation of excited vinyl radicals.

$$C_2H_3^{\cdot} + C_2H_3^{\cdot} \begin{cases} \longrightarrow C_2H_2 + C_2H_4 & (20) \\ \xrightarrow{+M} C_4H_6 & (21) \end{cases}$$

$$C_2H_3^{\cdot\dagger} \rightarrow C_2H_2 + H^{\cdot} \qquad (22)$$

The detection of methane, ethane, propane and propene indicates that methyl and ethyl radicals must be formed in the system. The yields of these minor products are sensitive to small additions of argon thus it is probable that their formation chain is initiated by excited vinyl radicals. A scheme which can account for these products is as follows:

$$C_2H_3^{\cdot\dagger} \rightarrow C_2H_2 + H^{\cdot} \qquad (22)$$

$$C_2H_4 + H^{\cdot} \rightarrow C_2H_5^{\dagger\cdot} \qquad (23)$$

$$C_2H_5^{\dagger\cdot} + H^{\cdot} \begin{cases} \rightarrow C_2H_6^{\dagger} \xrightarrow{+M} C_2H_6 \\ \rightarrow 2CH_3^{\cdot} \end{cases} \qquad (24)$$

$$CH_3^{\cdot} + C_2H_3^{\cdot} \xrightarrow{+M} C_3H_6 \qquad (25)$$

$$CH_3^{\cdot} + Sn(C_2H_3)_4 \rightarrow Sn(C_2H_3)_3C_2H_2 + CH_4 \qquad (26)$$

$$CH_3^{\cdot} + C_2H_3^{\cdot} \rightarrow CH_4 + C_2H_2 \qquad (27)$$

$$CH_3^{\cdot} + C_2H_5^{\cdot} \xrightarrow{+M} C_3H_8 \qquad (28)$$

$$C_2H_5^{\cdot} + C_2H_3^{\cdot} \xrightarrow{+M} C_4H_8 \qquad (29)$$

The sequence of reactions 23-25 which results in methyl radical formation has been suggested previously by Barker [13] and Cowfer [14]. The detection of moderate quantities of propene at high dilution in argon and oxygen indicates that this product may be formed by an unusual molecular elimination process of the type:

$$Sn(C_2H_3)_4^{*} \rightarrow SnC_2H_3CH + C_2H_2 + C_3H_6 \qquad (30)$$

TABLE 3

PUBLISHED VALUES FOR THE RATIOS OF THE COMBINATION (k_r) TO DISPROPORTIONATION (k_d) RATE CONSTANTS FOR VINYL RADICALS ·

System	k_r/k_d	Reference
a. Flash photolysis of vinyl iodide at 313 nm	2.50	10
b. Flash photolysis of vinyl iodide at 254 nm	0.40	10
c. Irradiation of a mixture of vinyl formate and acetaldehyde at > 300 nm	0.91	15
d. Decomposition of a mixture of vinyl iodide and bromide by sodium diffusion flame technique	0.50	16
e. Continuous photolysis of divinylmercury between 220-260 nm	50.00	12
f. Flash photolysis of divinyl ether at > 200 nm	Trace butadiene	17
g. Methane photosensitised decomposition of acetylene	0.33	18
h. Flash photolysis of tetravinyltin	0.27	This work

If it is assumed that all the products detected in high dilutions in oxygen result from molecular elimination then our data obtained under these conditions, can be used to estimate the ratio of the rate constants for the combination (k_r) and disproportionation (k_d) reactions of vinyl radicals. From Table 2, the yields due to molecular elimination and radical reactions, under high dilution conditions, may be apportioned. The rate constant ratio is estimated to be 0.27 from these figures. This value is compared to the other reported values in Table 3. The present ratio is in good agreement with those of Takita et al. [18] and Yamashita et al. [10].

	C_2H_4	C_2H_2	C_4H_6
Molecular elimination	1.01	1.05	0.05
Radical reactions	0.64	0.68	0.17

Nature of the photoexcited states of TET and TVT

As discussed previously, our data give evidence of two excited states, one quenchable the other not, produced in our experiments. Similar observations have been made by Borrell [1,2]. The unquenchable species is likely to be formed following a transition into a dissociative region of an upper electronic state, dissociation from this state being too rapid to allow time for collisional deactivation.

One difference between the TET and TVT experiments is that in the former argon did not appear to quench either photoexcited state of the parent molecule. This may be because a transition is possible from the quenchable excited state of TET to an unstable excited state. For such intersystem crossing to occur the molecule must be in a configuration common to both excited states, i.e. it must be able to exist at the "crossing point" of the two systems (easily pictured in terms of a potential energy diagram). Since argon can only remove small amounts of energy on collision, a fine step-ladder process occurs. Thus the excited molecule always has the possibility of being in or near the critical configuration. That argon did not remove the quenchable state, even when it was present in very large excess, indicates a high probability of intersystem crossing from the quenchable state. Sulphur hexafluoride is a very efficient collision partner removing relatively large amounts of energy per collision, thus it is possible that the de-excitation process is able to make the system 'jump' below the critical configuration before crossing can occur. Why this effect was not observed in the TVT experiments is not certain, but it may result from a low probability associated with intersystem crossing for this molecule.

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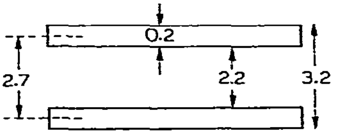
Appendix

(a). Estimate of extent of light absorption

For the present calculation the cell was split into two distinct regions. The first was an annulus, which fitted round the body of the lamp and whose measurements (cm) were the average of all the cells, thus:



Wall thickness = 0.15 cm
Volume of annulus = 10.3 cm^3

The area over which the irradiation occurred was averaged at the mean distance across the annulus, i.e. 53.44 cm^2. The second irradiated region was taken as equivalent to that in an imaginary cylinder at the end of the lamp with a volume of 13 cm^3 and length 1.5 cm. This zone had to be established in order to simply account for the volume of the septum cap device. The effective area of irradiation was taken at 2.7 cm diameter i.e. 5.73 cm^2.

M_0, for each region, was calculated from the initial concentration (M_{TET}) of TET in the cell i.e.

$$M_0 = M_{\mathrm{TET}} \frac{\text{Path length}}{\text{Total cell volume}}$$

The extinction coefficient was taken as the average over the absorption region (195-235 nm) calculated by a simple weighing technique using the spectra in Fig. 2; the result is 5.08×10^3 l mol^{-1} cm^{-1}. Finally n_Q was calculated from the total number of quanta per unit area obtained by uranyl oxalate actinometry [3] (5.79×10^{18} quanta are given out by lamp over whole cell), i.e.

$$n_Q = \frac{\Delta\lambda(\text{TET})}{\Delta\lambda(\text{Actinometer})} \cdot \frac{\text{No. of quanta}}{6.023 \times 10^{23}} \cdot \frac{\text{Fraction of light}}{\text{Effective area}}$$

where $\Delta\lambda$ refers to the wavelength range of absorption, $\Delta\lambda$ (actinometer) = 290 nm. The fraction of light through each part of the cell was simply related to the relative cross-sectional areas of the two irradiated regions, i.e. the fraction through the annulus is 0.92 and the end is 8.03×10^{-2}.

With this data the percentage of the molecules absorbing light (α) can be calculated for each region using the initial equation; the results obtained were (a) annulus 10.84% and (b) end cylinder 8.37%. For the purposes of averaging the two regions and to take into account the tap stem, which is connected to the annulus, the volume of this region was taken to be 11 cm^3. (An average measured cell volume of 24 cm^3 was used in all calculations). The result of this averaging gives a total cell absorption of 9.5%.

When this calculation was applied to the results obtained by Cuff [3] for the flash photolysis of dimethylmercury (DMM) and tetramethyllead (TML) the decomposition, assuming a quantum yield of unity, obtained was slightly higher than the experimental result he obtained at high dilution of argon. Now it is known with some certainty that two methyl units are lost with each DMM and four methyls with each TML molecule decomposed thus the TET calculations were normalised to Cuff's results. The necessity for this procedure can be explained largely by the somewhat crude approximations used in the dividing of the cell regions and by the fact that part of the thimble of the cell is constructed of a graded seat of indeterminate optical properties. The normalisation procedure required α, for both regions, to be multiplied by the factor 0.89; thus the best estimation of the TET molecules absorbing light, assuming a quantum yield of unity and using a typical initial concentration (5.21×10^{-7} mol), is 8.5%.

(b). Estimation of dilution ratio at which excited radicals are significantly deactivated

The number of collisions of an ethyl radical with a species A per second is given by:

$$Z_{\mathrm{Et/A}} = n_{\mathrm{A}} \frac{\sigma^2_{\mathrm{Et/A}}}{\mu^{0.5}_{\mathrm{Et/A}}} (8\pi \mathrm{RT})^{0.5}$$

where n_{A} is the concentration of A in mol l^{-1}, $\sigma_{\mathrm{Et/A}}$ is the collision diameter between the ethyl radical and A, and μ is the reduced mass. For the present calculation, collisions between the radicals, the substrate, the diluent (argon) and the stable products are considered. The dilution at which the decomposition yield begins to level off is when the probability of deactivation and radical reaction are equal to the probability of reaction with the substrate, i.e.

$$Z_{\mathrm{Et^*/TET}} = \frac{1}{x} Z_{\mathrm{Et/Ar}} + \frac{1}{y} (Z_{\mathrm{Et/C_2H_4}} + Z_{\mathrm{Et/SnEt_2H_2}}) + Z_{\mathrm{Et/Et}}$$

where x is the number of collisions of the radical with argon to ensure deactivation. All the stable products were considered to have the same number of deactivating collisions, i.e. y, because they can be considered to behave as simple hydrocarbons.

The only problem with this calculation lies in the definition of x and y since no previous data are available on the deactivation of ethyl radicals. Callear

[19] has investigated total relaxation by argon and ethane of excited methyl radicals formed in the flash photolysis of dimethylmercury; he estimated that 200 and 30 collisions respectively were necessary for this process. Now deactivation corresponds to removal of part of the excitation energy of the radical and is thus expected to occur more rapidly, i.e. with less collisions, than full vibrational relaxation. In the flash photolysis of DMM and TML [3] excited methyl radicals are formed and the decomposition yields in both cases falls on increasing dilution until a point is reached at which the yields are dilution independent. From a detailed study of the relative formation of the secondary products, ethylene and acetylene, it was postulated that the more excited the radicals recombining to form ethane the greater the probability of subsequent formation of the unsaturated products. That dilution below which the minor products began to rise rapidly was considered to be when the probability of an excited methyl radical recombination was equal to the probability of deactivation of the excited radical. Thus:

$$Z_{\mathrm{CH_3/CH_3}} = \frac{1}{30a} Z_{\mathrm{CH_3/M}} + \frac{1}{200a} Z_{\mathrm{CH_3/Ar}}$$

where a is the fraction of the total number of relaxing collisions needed for deactivation and M is TML or DMM. The efficiency of the metal alkyls for deactivating the methyl radicals was assumed to be equal to that for ethane. The value of a was calculated with a knowledge of the dilution ratio below which the minor products became increasingly important, the average result was 0.48 (averaged from DMM a 0.488 and 0.498, TML a 0.492). In order to carry out the calculation in the ethyl radical system, we have assumed that the fraction a was reduced by the ratio of the number of internal degrees of freedom of the methyl to ethyl radicals, i.e. a 0.19. This is because the post-decomposition energy in both radicals is approximately equal and thus the average energy per degree of freedom is correspondingly less in ethyl than methyl radicals. The values of the unknown x and y are simply $200a$ and $30a$ respectively, i.e. 38 and 6 collisions with argon and stable products are necessary to deactivate, in a reactive sense, an excited ethyl radical.

Using the data given in Table 4 (where the collision diameter is approximated to the most appropriate hydrocarbon [20]), the dilution ratio was calculated utilising these effective number of collisions, the result obtained for the ratio at which the yields begin to change is 60.

TABLE 4

COLLISION DIAMETERS FOR SPECIES IN TET AND TVT

Species	Appropriate hydrocarbon	Collision diameter/nm
Ethyl radical	Ethane	0.442
Vinyl radical	Ethylene	0.423
TET	≈ $n\text{-}C_9H_{20}$	0.793
TVT	≈ $n\text{-}C_9H_{20}$	0.790
Argon		0.342
$SnEt_2H_2$	≈ $n\text{-}C_9H_{20}$	0.790
$SnVin_2$	Estimated	0.600

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