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FT-IR study of the gas phase thermal decomposition of dimethyldivinyltin in the presence of oxygen

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Abstract

The thermal decomposition of dimethyldivinyltin (DMDVT) in the presence of oxygen (15.5:1 oxygen:DMDVT molar ratio) has been investigated by FT-IR in the temperature range 543–613 K. The major permanent products from the reaction are methane, ethene and carbon dioxide together with smaller amounts of acetylene, carbon monoxide and water vapour. In addition, transient quantities of methanol, formaldehyde and acetaldehyde are also formed. The loss of DMDVT from the gas phase follows zero-order kinetics with observed rate constants varying from 6.18×10^{-9} mol dm^{-3} s^{-1} at 543 K to 2.30×10^{-7} mol dm^{-3} s^{-1} at 613 K. Arrhenius analysis gives the relationship $\ln k_{obs} = 9.817 - 15.30 \times 10^3/T$, which yields a value of 127 kJ mol^{-1} for the activation energy, E_a, much lower than typical values for the Sn–C bond dissociation energy. The data are interpreted in terms of surface-mediated rather than homogeneous gas-phase reactions, with the dissociative chemisorption of DMDVT being the rate-determining step.

Introduction

The oxidative thermal decomposition of organotin compounds is an important process in the deposition of thin films of tin(IV) oxide by MOCVD. However, there exists very little understanding of the fundamental chemistry involved. The most widely studied compound is tetramethyltin, which has been studied by several groups of workers [1–3]. Two of these studies [1,2] are rather old and are not entirely satisfactory. The third [3] was carried out in a toluene carried flow system from 803–941 K using total pressures of 10.6 to 52.4 mmHg. The kinetic data was consistent with a first-order reaction in which tetramethyltin molecules undergo homolytic tin–carbon bond fission in the gas phase. The resultant methyl radicals afforded a typical product distribution comprising methane, ethane, ethene and ethylbenzene. The activation energy of the process was determined from the Arrhenius plot to be 64.5(10) kcal mol^{-1} (270 ± 4 kJ mol^{-1}). This value was

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* Dedicated to Professor Alwyn G. Davies in recognition of his distinguished contributions to organometallic chemistry.

considered to correspond to the first tin–carbon bond fission as the rate-determining step, and hence was considered to be a good approximation of the bond dissociation energy, $D[(CH_3)_3Sn{-}CH_3]$. No appreciable heterogeneous reaction could be detected, *i.e.* all the decomposition was considered to occur in the gas phase.

We have previously reported preliminary details of a FT-IR study of the thermal decomposition of tetramethyltin in the presence of a stoichiometric excess of oxygen for exhaustive oxidation to tin(IV) oxide, carbon dioxide and water vapour. Somewhat surprisingly, we found that decomposition under these conditions does not produce the thermodynamically most favourable products, but rather methane and carbon dioxide are formed in a 3:1 molar ratio. Further, kinetics for the disappearance of tetramethyltin are zero-order indicating a heterogeneous, surface-mediated process rather than a homogeneous gas-phase reaction [4].

In this paper we describe a similar FT-IR study of the thermal decomposition of dimethyldivinyltin (DMDVT), $(CH_3)_2$,$Sn(CH{=}CH_2)_2$, in the presence of a large excess of oxygen.

Experimental

The experimental arrangement employed for the infrared studies is a simple one, and comprises an infrared gas cell connected to a conventional vacuum line system operating at a backing pressure of $< 10^{-5}$ millibar. The body of the cell was of Pyrex glass, and KBr windows were adhered to the polished parallel ends of the cell using Picene adhesive giving a vacuum-tight seal. Heating of the cell was accomplished by using conventional heating tape wound uniformly along the cell body, and controlled by a Eurotherm temperature controller and type K thermocouple positioned in the interior of the centre of the cell. The cell windows and Picene seals were maintained at a moderately low temperature by water cooling.

For a kinetic run, the cell was placed in the sample compartment of the Nicolet 5DXB FT-IR spectrometer whilst still connected to the vacuum line system, evacuated and the appropriate quantity of the gas mixture to be examined introduced at ambient temperature. The heating cycle was initiated (usually rapid heating to the desired temperature after which isothermal conditions were maintained). Spectra were recorded (10 scans per spectrum) at appropriate intervals throughout the run. Gas-phase concentrations of reactants and products were measured by observing the absorbance changes in infrared bands characteristic of each component and calibrated using known concentrations.

Results and discussion

1. Product speciation

The infrared spectrum of DMDVT in the gas phase at ambient temperature is shown in Fig. 1(a). The spectrum is virtually identical to a composite of the individual spectra of the two homoleptic compounds TMT and TVT, as the numerical data listed in Table 1 show.

Thermal decomposition studies were carried out using mixtures containing approximately a 15.5:1 oxygen:DMDVT molar ratio, ie greater than that required

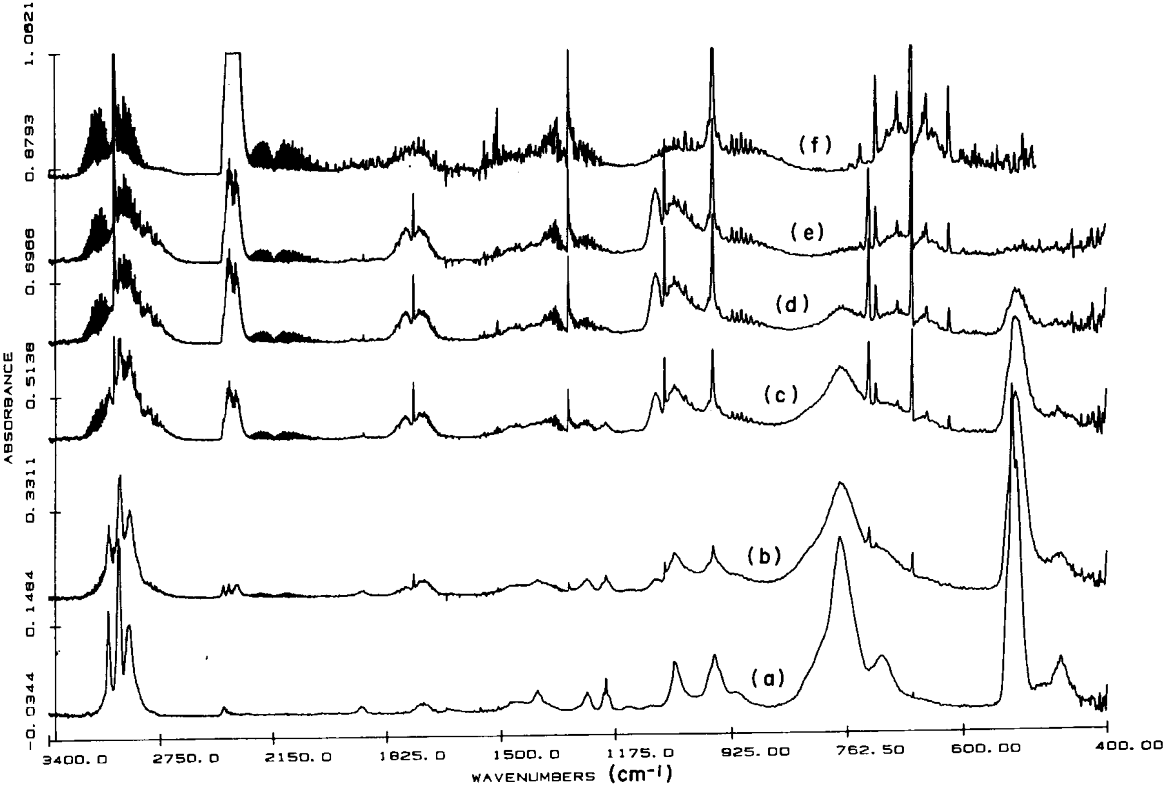


Fig. 1. Infrared spectra in the range 400–3400 cm^{-1} of (a) DMDVT in the gas phase at ambient temperature, after heating a 15.5:1 mixture of oxygen and DMDVT at 558 K for 12 min (b), and futher heating at 593 K for 20 min (c), 30 min (d), 40 min (e), and 160 min (f).

Table 1

Infrared spectral data ($\mathrm{cm^{-1}}$) for dimethyldivinyltin in the gas phase in the range 400–3400 $\mathrm{cm^{-1}}$ (with corresponding data [a] for tetramethyltin (TMT) and tetravinyltin (TVT) in parentheses)

Band position	Assignment
464 (m) (TVT 469)	$\delta(\mathrm{CH})_{\mathrm{wag}}(\mathrm{Sn{-}C(H){=}C})$
530 (s) (TVT 528; TMT 529)	$\nu(\mathrm{Sn{-}C})$
713 (m)	?
771 (s) (TMT 771)	$\rho(\mathrm{CH_3})$
948 (m) (TVT 950)	$\delta(\mathrm{CH_2})_{\mathrm{wag}}(\mathrm{-C{=}CH_2})$
1003, 1008 (m) (TVT 1005)	$\rho(\mathrm{CH_2})(\mathrm{-C{=}CH_2})$
1200 (m) (TMT 1200)	$\delta_{\mathrm{s}}(\mathrm{CH_3})$
1254 (m) (TVT 1244)	$\rho(\mathrm{CH})(\mathrm{-C(H){=}C})$
1396 (m) (TVT 1389)	$\delta(\mathrm{CH_2})_{\mathrm{sciss}}$
1718 (w) (TMT 1717)	530 + 1200
1896 (w) (TVT 1897)	2 × 948
2382 (w) (TMT 2384)	2 × 1200
2926 (s) (TMT 2919)	$\nu_{\mathrm{s}}(\mathrm{CH_3})$
2945 (s) (TVT 2934)	$\nu_{\mathrm{s}}(\mathrm{CH_2})(\mathrm{C{=}CH_2})$
2981 (s) (TVT 2976)	$\nu_{\mathrm{s}}(\mathrm{CH})(\mathrm{-C(H){=}C})$
2988 (s) (TMT 2991)	$\nu_{\mathrm{as}}(\mathrm{CH_3})$
3046 (s) (TVT 3046)	$\nu_{\mathrm{as}}(\mathrm{CH_2})(\mathrm{C{=}CH_2})$
3167 (s) (TVT 3157)	2 × 1580

[a] Data from W.F. Edgell and C.H. Ward, *J. Am. Chem. Soc.*, 77 (1955) 6486, and G. Masetti and G. Zerbi, *Spectrochim Acta, Sect. A*, 26 (1970) 1891.

for the stoichiometric total oxidation according to eq. 1:

$$(\mathrm{CH_3})_2\mathrm{Sn}(\mathrm{CH{=}CH_2})_2 + 11\mathrm{O_2} \longrightarrow \mathrm{SnO_2} + 6\mathrm{CO_2} + 3\mathrm{H_2O} \qquad (1)$$

where the only expected gas-phase products would be CO_2 and H_2O. That this is not the case and that the decomposition follows a much more complex course is illustrated in Fig. 1 which shows a series of spectra recorded during the decomposition of DMDVT in the presence of oxygen at 593 K, and which are typical of the other kinetic runs carried out in the temperature range 553–613 K. As the reaction proceeds, the bands due to DMDVT are observed to gradually decay, and are totally absent from the spectrum after heating for 40 min at 593 K. Bands due to two types of product are observed: (*i*) those which increase in intensity during the duration of the run, and (*ii*) those which increase to a maximum and subsequently disappear from the spectrum. The identified products together with their characteristic spectral features are listed in Table 2. The major permanent products from the reaction are methane, ethene and carbon dioxide together with smaller amounts of acetylene, carbon monoxide and water vapour. In addition, transient quantities of methanol, formaldehyde and acetaldehyde are also formed. These products are still present after all the DMDVT is lost from the gas phase, but are themselves removed after prolonged heating. Authentic spectra of methanol, methane, acetaldehyde, acetylene and ethene, together with a typical product mixture spectrum are shown in Fig. 2. Thus, as observed with Me_4Sn, only partial oxidation of DMDVT occurs under these conditions. Of the products derived from DMDVT, methane, CO_2, CO, methanol and formaldehyde arise from the methyl groups, whilst ethene, acetylene and acetaldehyde arise from the vinyl groups.

Table 2

Principal infrared features of reaction products [a] (cm^{-1}) (with literature values [b] in parentheses)

Product	Band position	Band form	Assignment
CH_4	3017.8(3018.9)	P, Q, R	deg. str.
	1305.9(1306.2)	P, Q, R	deg. def.
CH_3OH	2844.6(2844)	P, Q, R	$\nu_s(CH_3)$
	1032.9(1033)	P, Q, R	$\nu(CO)$
H_2CO	2843(2843)		$\nu_{as}(CH_2)$
	1745.7(1746.1)	P, Q, R	$\nu(CO)$
CO_2	2349	P, –, R	$\nu_{as}(CO_2)$
	668.4(667.4)		$\delta(CO_2)$
CO	2144(2144)	P, –, R	$\nu(CO)$
C_2H_4	3107(3105.5)	P, –, R	$\nu_{as}(CH_2)$
	1443.3(1443.5)	P, Q, R	$\delta(CH_2)_{sciss}$
	950(949.3)	P, Q, R	$\delta(CH_2)_{wag}$
C_2H_2	730.2(730.3)	P, Q, R	$\delta(CH)$
CH_3CHO	2824(2822)		$\nu(CH)$
	1746.3(1743)	P, Q, R	$\nu(CO)$
	509(509)	P, Q, R	$\delta(CCO)$

[a] Small amounts of water vapour are also formed. [b] Data from Tables of molecular vibrational frequencies consolidated, Volume 1, T. Shimanouchi, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (US)*, 39, June 1972, and references therein.

2. *Kinetic data*

Plots of the absorbance of the tin–carbon stretching band *versus* time for runs carried out at temperatures in the range 553–613 K are all linear over the regions of isothermal conditions (Fig. 3). The solid lines on these plots are the least-squares computed linear best fits to the data. These data show that under these conditions the reaction is zero-order in DMDVT in all cases. The onset of product formation coincides with the initiation of DMDVT reaction. Rate constant data for these experiments are tabulated in Table 3. The zero-order rate constants for the loss of DMDVT range from 6.18×10^{-9} mol dm^{-3} s^{-1} at 543 K to 2.30×10^{-7} mol dm^{-3} s^{-1} at 613 K. The Arrhenius plot for these data is shown in Fig. 4, and least squares analysis gives the relationship $\ln k_{obs} = 9.817 - 15.30 \times 10^3/T$ (correlation coefficient 0.9956) with a calculated activation energy, E_a, for the rate-determining step of the reaction of 127 kJ mol^{-1} and an A value of 1.83×10^4.

3. *Mechanistic interpretation*

Both the zero-order loss of DMDVT from the gas phase and the low value of the activation energy, which is significantly lower than typical values of the tin-carbon bond dissociation energy (*e.g.* for Me_4Sn, $D[(CH_3)_3Sn{-}CH_3] = 278$ kJ mol^{-1}), indicate that the thermal decomposition of DMDVT in the presence of oxygen is a surface-mediated reaction which occurs on the walls of the infrared cell, rather than a homogeneous gas-phase reaction. For the reaction to appear zero-order in DMDVT, the number of reaction sites on the surface must be much lower than the concentration of DMDVT in the gas phase so that the reaction sites are constantly replenished. That the activation energy is significantly lower than the tin–carbon bond dissociation energy indicates that the reaction does not proceed via tin–carbon bond dissociation immediately prior to adsorption. Rather,

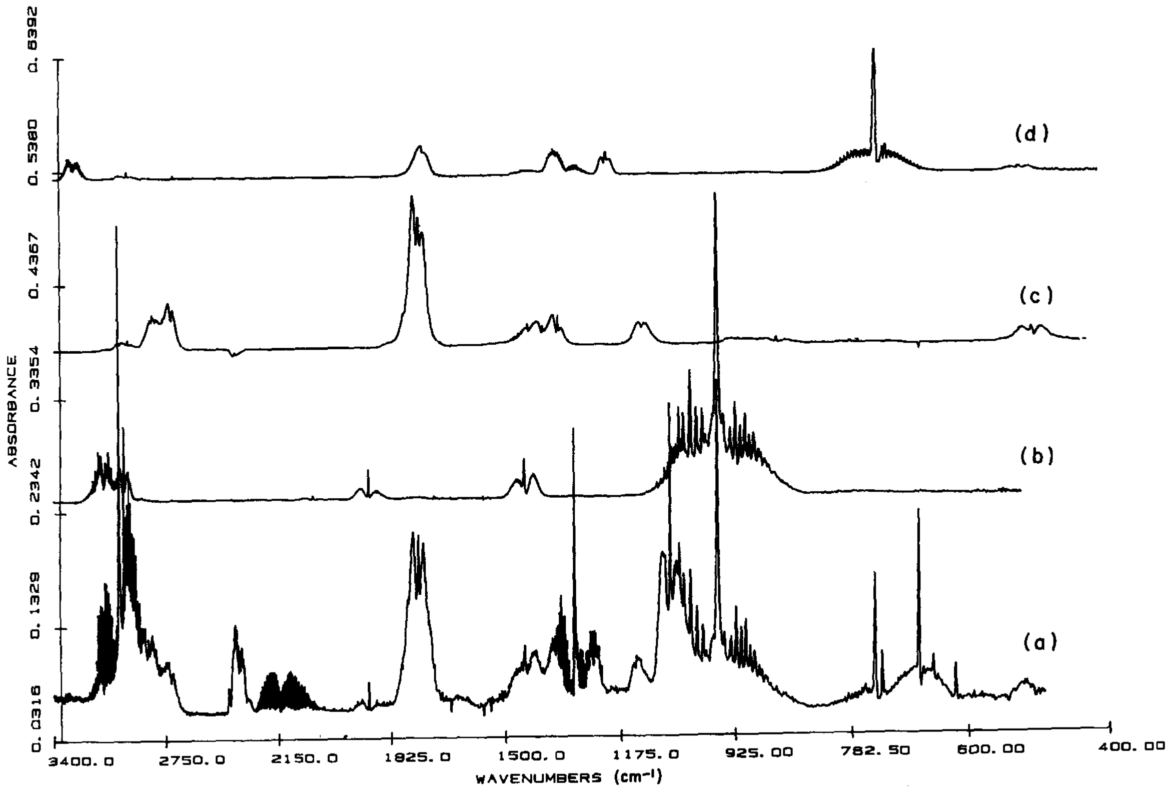


Fig. 2. Infrared spectra of (a) a typical product mixture together with spectra of ethene (b), acetaldehyde (c), acetylene (d), methane (e), and methanol (f).

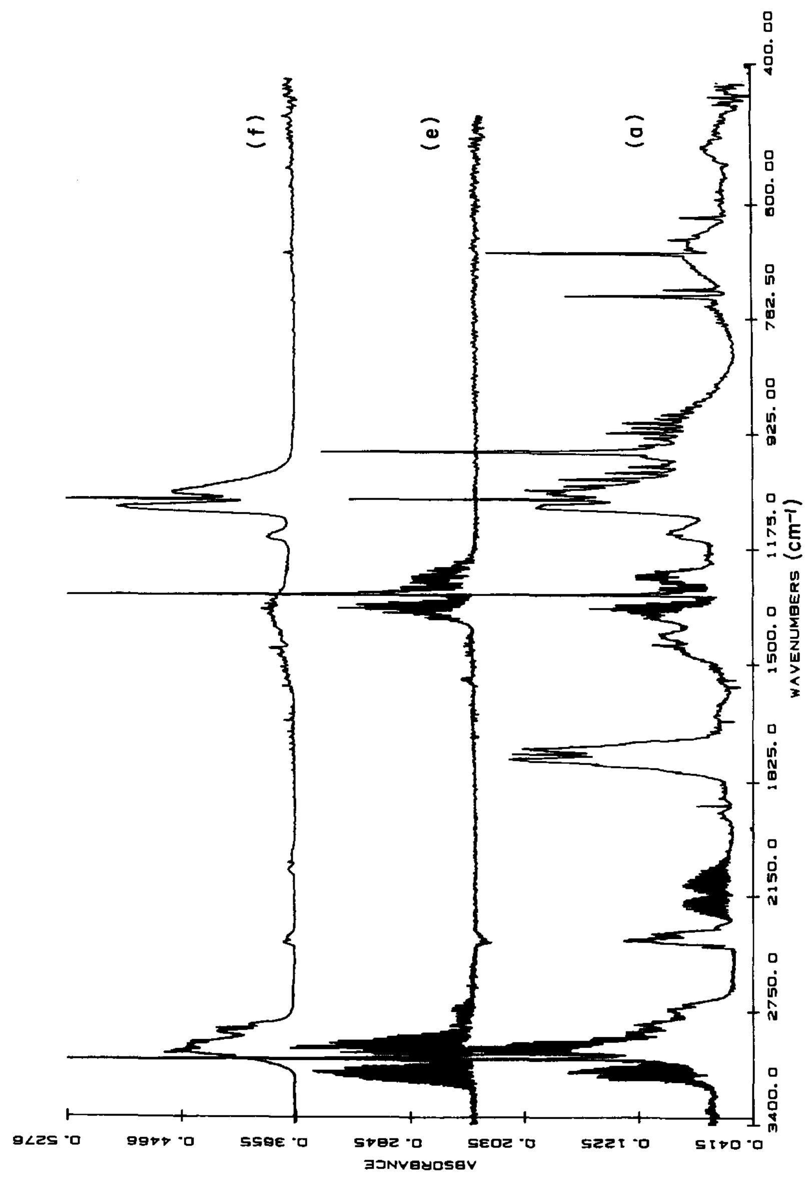


Fig. 2. (continued).

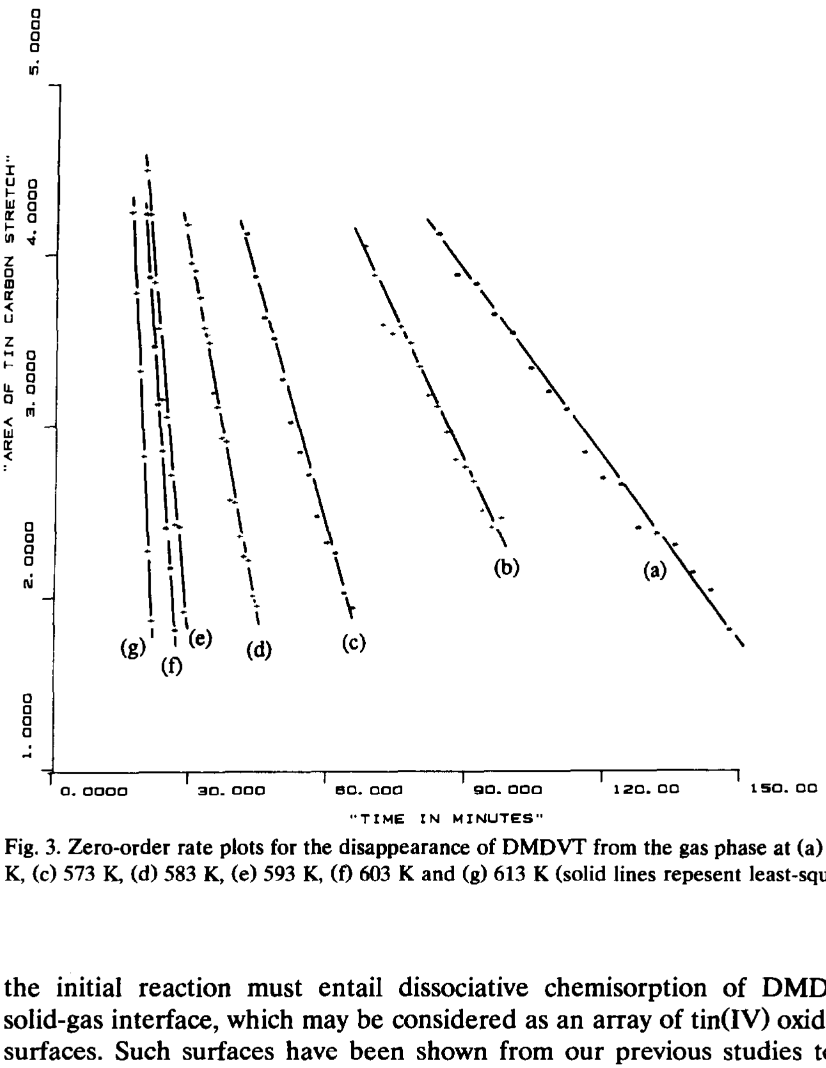


Fig. 3. Zero-order rate plots for the disappearance of DMDVT from the gas phase at (a) 553 K, (b) 563 K, (c) 573 K, (d) 583 K, (e) 593 K, (f) 603 K and (g) 613 K (solid lines repesent least-squares fits).

the initial reaction must entail dissociative chemisorption of DMDVT at the solid-gas interface, which may be considered as an array of tin(IV) oxide crystallite surfaces. Such surfaces have been shown from our previous studies to be a very

Table 3

Rate constant data for the disappearance of dimethyldivinyltin

Temperature (K)	Rate constant (K_{obs} mol dm^{-3} s^{-1})($\times 10^9$)
543	6.18
553	16.70
563	26.13
573	43.50
583	67.78
593	131.5
603	163.7
613	229.7

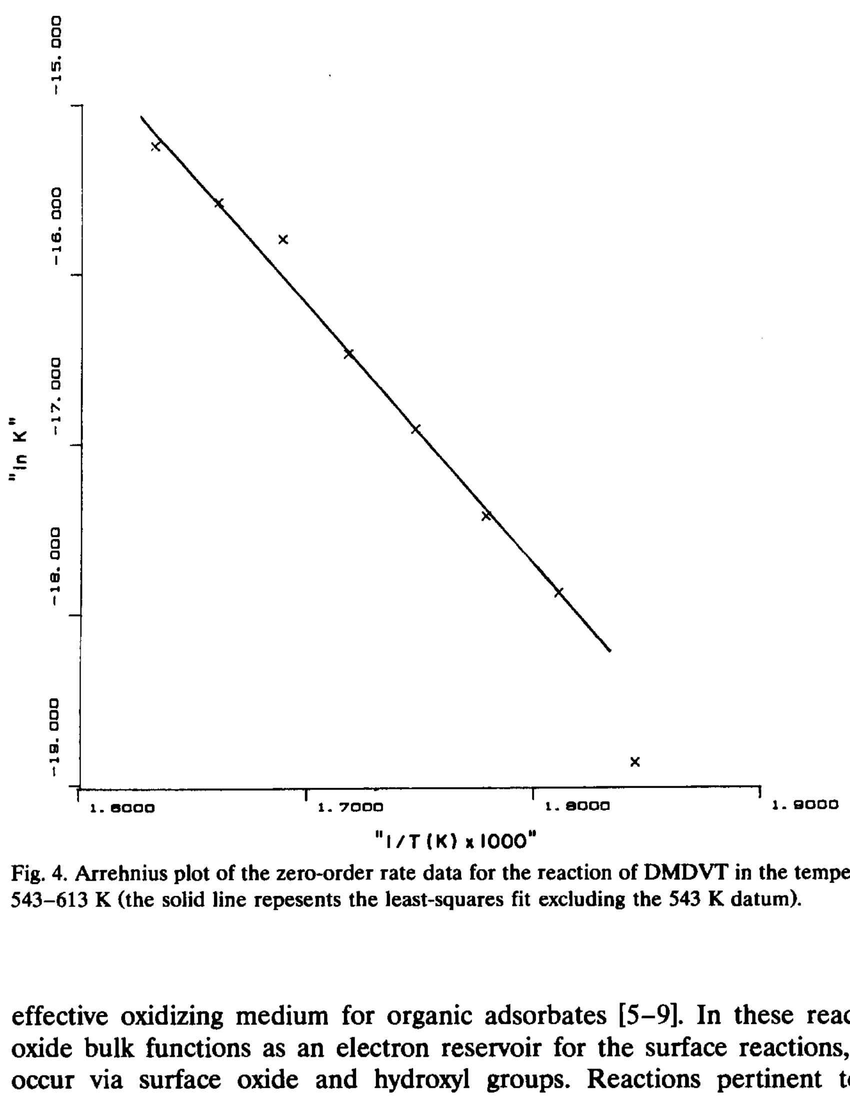
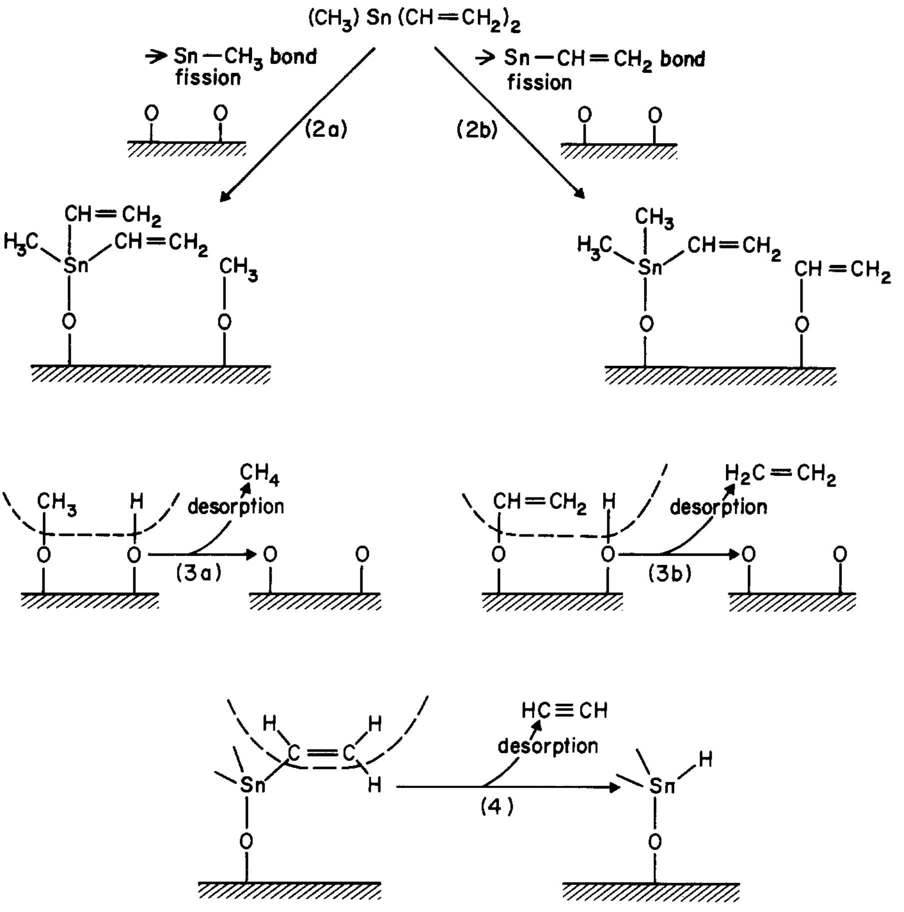


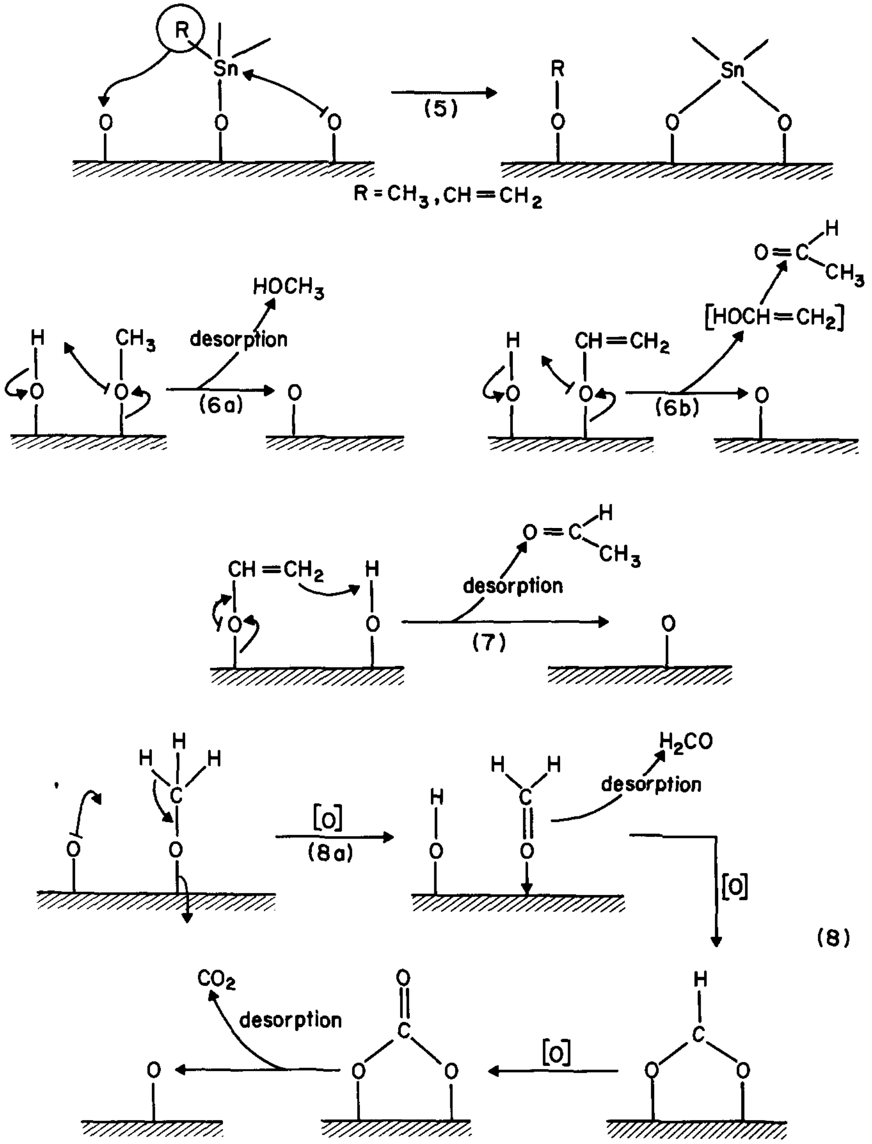
Fig. 4. Arrehnius plot of the zero-order rate data for the reaction of DMDVT in the temperature range 543–613 K (the solid line repesents the least-squares fit excluding the 543 K datum).

effective oxidizing medium for organic adsorbates [5–9]. In these reactions, the oxide bulk functions as an electron reservoir for the surface reactions, which all occur via surface oxide and hydroxyl groups. Reactions pertinent to product formation in the present case are collected in Scheme 1. Since the products arising from both methyl and vinyl groups are produced simultaneously, there appears to be little or no selectivity between the two groups either during the initial dissociative chemisorption or the subsequent surface reactions. Thus, initial dissociative chemisorption will afford surface-bound $\{(CH_3)_2(CH_2{=}CH)SnO{-}\}$, $\{CH_3(CH_2{=}CH)_2SnO{-}\}$, $\{H_3CO{-}\}$, and $\{CH_2{=}CHO{-}\}$ species arising from the initial dissociative chemisorption involving either $Sn{-}CH_3$ (eq. 2a) or $Sn{-}CH{=}CH_2$ (eq. 2b) bond cleavage at adjacent double surface oxygen sites. Loss of the remaining groups from the surface-anchored triorganotin species is most probably via reaction with adjacent surface-bound hydroxyl groups giving rise to methane (from the methyl groups) (eq. 3a) and ethene (from the vinyl groups) (eq. 3b) as major products. The small amount of acetylene appears to be formed via elimination from vinyltin species (eq. 4). Further surface $\{H_3CO{-}\}$, and $\{CH_2{=}CHO{-}\}$ species may be formed as a result of group transfer from the surface triorganotin species to a



Scheme 1.

neighbouring surface oxygen (eq. 5). The oxygen-containing products arise from the protolytic cleavage or oxidation of the surface {H_3CO–} and {CH_2=CHO–} species. Thus, protolytic cleavage (by surface hydroxyl groups) of surface {H_3CO–} groups affords methanol (eq. 6a), whereas protolysis of surface {CH_2=CHO–} groups will give acetaldehyde either directly (eq. 7) or following tautomeric rearrangment of HOCH=CH_2 (eq. 6b). The oxidation of surface {H_3CO–} groups is facile, and leads to formaldehyde (eq. 8a). The ultimate surface product formed in the oxidation of organic adsorbates such as these is always surface carbonate (*e.g.* eq. 8), and it is the ready dissociative desorption as CO_2 from surface carbonate at elevated temperatures which is responsible for the large amount of CO_2 observed.



Scheme 1. (continued).

Acknowledgements

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