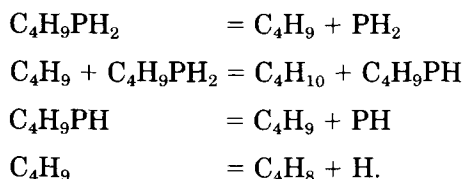


Pyrolysis of Tertiarybutylphosphine

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The reaction mechanism for the pyrolysis of tertiarybutylphosphine (TBP) has been studied in an atmospheric pressure flow tube reactor using a time-of-flight mass spectrometer to analyze the gaseous products. D₂ was used as the carrier gas in order to label the reaction products. The temperature and time dependence of TBP pyrolysis were investigated above a silica surface, which was found to have no effect on TBP decomposition. However, the pyrolysis rate and products are strongly dependent on the input TBP concentration, suggesting the TBP pyrolysis involves second order reactions. A simple free radical mechanism model is proposed which includes 4 major reactions:



Arrhenius parameters for these reactions are reported.

Key words: Tertiarybutylphosphine, OMVPE (MOCVD), pyrolysis

INTRODUCTION

Organometallic vapor phase epitaxy (OMVPE)¹ is now one of the most promising techniques for large scale production of III/V semiconductor materials which are vital for optoelectronic devices, ultra-high speed transistors, and high performance solar cells.² In OMVPE, the group III precursors are organometallic compounds, and the group V precursors are typically hydrides. The former usually pyrolyze at temperatures relatively lower than for the latter. Therefore, high V/III ratios are required to obtain the best morphologies and electrical and optical properties.³ Another problem with the hydrides, specifically arsine and phosphine, is their extreme toxicity. They are stored in high pressure cylinders exacerbating the potential hazard. The solution to these problems is a key to enabling the widespread use of OMVPE for commercial production.

The search for less or non-toxic group V sources is difficult but imperative. The requirements for an OMVPE group V source include high vapor pressure, low temperature stability, pyrolysis at temperatures of around 400° C, no parasitic reactions with group III sources, and little carbon incorporation.⁴ Although detailed knowledge of the growth reactions is still inadequate it is believed that in order to reduce carbon incorporation one or more hydrogen atoms bonded to the group V element is required.⁵

Recently, tertiarybutylphosphine (TBP) has been used successfully to grow InP epitaxial layers with

no deleterious gas phase reactions, producing layers which have excellent morphologies and little, if any, additional carbon incorporation as compared to epitaxial layers grown using phosphine.⁶⁻⁷ The full widths at half-maximum of the main 4K photoluminescence peaks for the InP layers grown using TBP have been found to be as low as 1.3 meV as compared to the value of 1.1 meV obtained using phosphine.⁸ However, the toxicity of TBP is much less than for phosphine; the LC₅₀ is over 1000 ppm as compared to the value of 11 ppm for phosphine.^{4,9} This successful beginning may lead to even better non-hydride group V precursors. To improve the OMVPE process and to allow the development of advanced precursor molecules, it is important that the growth mechanisms using the new group V sources be fully understood.

This paper represents the first step in an investigation of OMVPE growth using TBP, namely an investigation of TBP pyrolysis. The reactions were studied employing mass spectrometric analysis of the effluent gas with deuterium used as the carrier gas to label the reaction products. Two related papers dealing with the OMVPE growth mechanism for GaP using TBP and TMGa, and the TBP pyrolysis using a deuterated source will be published elsewhere.¹⁰⁻¹¹

EXPERIMENTAL

The experiments were carried out in an atmospheric pressure flow tube reactor using a time-of-flight mass spectrometer, as described previously.¹² D₂, instead of H₂, was used as the carrier gas in order to label the products and to distinguish be-

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tween reactant/reactant and reactant/ambient reactions.

Electronic Grade TBP was supplied by American Cyanamid Company and the D_2 ambient gas was Research Grade from Air Products and Chemicals, Inc. The reactor consists of a silica tube of 0.4 cm ID in a furnace with a hot zone 41.5 cm long. To study the effects of surface on the TBP pyrolysis the reactor was packed with silica chips to increase the surface area to approximately 24 times that of the unpacked tube.

The time dependence of TBP decomposition for concentrations between 0.9 and 10% (5.7–63.5 Torr, in Salt Lake City) in a D_2 ambient was studied at 450° C to determine the overall reaction order. The temperature dependence of TBP decomposition, as well as the partial pressures of the decomposition products, was then studied for concentrations between 0.2 and 10%. For the former experiments the flow velocity was varied between 2 and 40 cm/sec, and for the latter experiments a constant flow rate of 40 sccm, corresponding to a flow velocity at STP of 5.3 cm/sec, was employed. Such flow velocities are typical of those used in OMVPE reactors, but the reaction times were intentionally longer than in real OMVPE reactors. Downstream from the reactor tube, the effluent flow was sampled using a mass spectrometer through an adjustable leak.

The relative abundances of the major peaks in the mass spectrum of a 5% concentration of TBP in D_2 , at an ionization energy of 70 eV, are given in Table I. The principal peak appears at $m/e = 57$ corresponding to $C_4H_9^+$, and the parent peak occurs at $m/e = 90$ with an intensity of about 20% the principal peak. When TBP decomposes, none of the products have significant contributions at m/e values of either 57 or 90. The sum of the intensities of the peaks at 57 and 90 is used to measure the TBP concentration. The pyrolysis products include isobutane (C_4H_{10}), isobutene (C_4H_8), phosphine (PH_3), and hydrogen (H_2). The concentrations were measured using the interference-free peaks at m/e values of 43, 56, 34, and 2, respectively.¹³ The ionization cross-section for each molecular species is estimated to be the sum of the ionization cross-sections of the constituent atoms.¹⁴

Table I. Relative Abundances of Species in the Mass Spectrum of 5% TBP in D_2 with an Ionization Energy of 70 eV

m/e	Ionic Species	Relative Abundance
27	$C_2H_3^+$	13.4
29	$C_2H_5^+$	47.8
39	$C_3H_3^+$	16.9
41	$C_3H_5^+$	54.8
45	CH_2P^+	6.9
47	$CH_2PH_2^+$	6.3
55	$C_4H_7^+$	6.3
57	$C_4H_9^+$	100.0
58	$C_4H_{10}^+$	6.5
75	$C_3H_6PH_2^+$	13.9
88	$C_4H_9P^+$	3.0
90	$C_4H_9PH_2^+$	20.2

RESULTS

The partial pressure of TBP (P_{TBP}) undecomposed after passing through the reactor tube at 450° C is shown in Fig. 1 as a function of average residence time (t) in the tube for various input TBP pressures (P_{TBP}^0). The decomposition rate is dependent on P_{TBP}^0 , as indicated by the different values of $t_{1/2}$, defined as the residence time needed to reduce the partial pressure to 50% of P_{TBP}^0 . The measured values of $t_{1/2}$ increase from 9 to 14 sec as P_{TBP}^0 decreases from 63.5 to 5.7 Torr (10% to 0.9%); the pyrolysis rate increases at higher concentrations. The variation of $t_{1/2}$ indicates the overall pyrolysis reaction of TBP is not first order.¹⁵

The data in Fig. 1 are then used to obtain the curves in Figs. 2a and 2b, assuming first and second order reaction kinetics respectively. For an input concentration of 0.9%, the first order assumption gives a straight line as shown in Fig. 2a, indicating the decomposition is nearly of first order.¹⁵ For a concentration of 10% the data more nearly correspond to a straight line in Fig. 2b, indicating the decomposition is nearly of second order.¹⁵ For the intermediate concentration (5%) the data fit neither the first nor the second order assumption, because the decomposition of TBP changes from nearly first order to nearly second order as the input partial pressure of TBP increases. These results differ from the first order decomposition of phosphine observed throughout this range of concentrations.¹⁶

The percentage of TBP decomposition is shown versus temperature at a constant flow rate of 40 sccm in Fig. 3 for concentrations of 0.9, 5, and 10% in an unpacked silica tube, as well as for the 5% concentration in a packed tube. The decomposition of TBP is enhanced at higher input concentrations, which corresponds to the shift of the reaction from first to second order. Increasing the surface area in the reactor tube had almost no effect on the decomposition. Thus, TBP pyrolysis is predominantly homogeneous in the presence of an SiO_2 surface in contrast to phosphine pyrolysis which is predominantly heterogeneous.¹⁷ The pyrolysis temperature

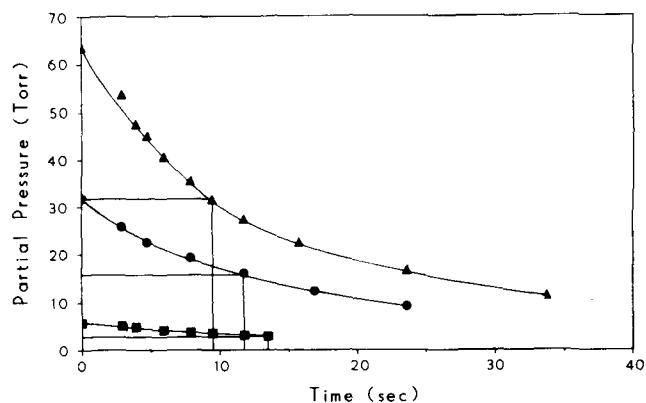


Fig. 1 — Unpyrolyzed TBP concentration vs residence time at 450° C, with initial TBP concentrations of 10% (\blacktriangle), 5% (\bullet), and 0.9% (\blacksquare). The values of $t_{1/2}$ are indicated for each concentration. The solid curves were drawn to fit the data.

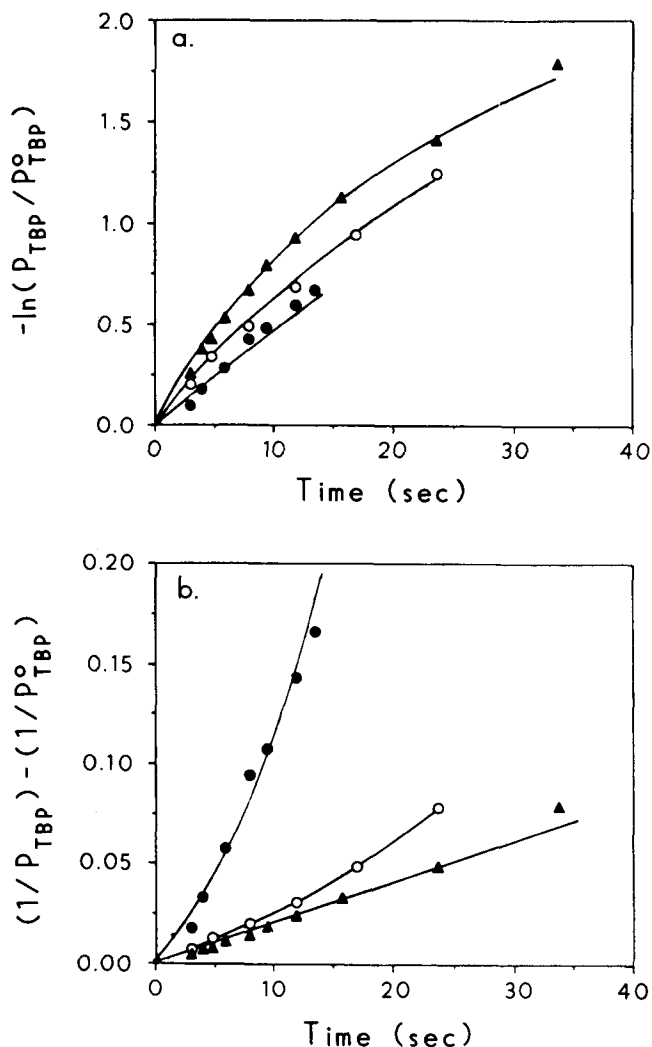


Fig. 2 — Plots of $-\ln(P_{\text{TBP}}/P_{\text{TBP}}^0)$ vs time (a) and $1/P_{\text{TBP}} - 1/P_{\text{TBP}}^0$ vs time (b), assuming first and second order reaction kinetics. Initial TBP concentrations were 10% (▲), 5% (○), and 0.9% (●).

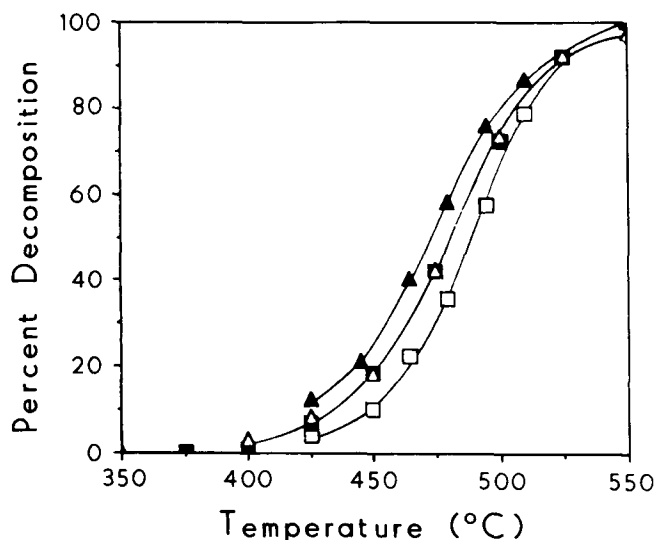


Fig. 3 — TBP decomposition versus temperature with low SiO_2 surface areas at initial TBP concentrations of 10% (▲), 5% (△), and 0.9% (□). Data for a TBP concentration of 5% (■) with a high SiO_2 surface area are also included.

for TBP is approximately 200°C lower than for phosphine.

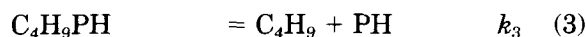
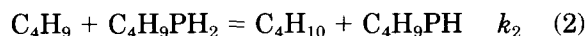
The temperature dependence of the pyrolysis products for TBP concentrations of 0.2, 0.9, 5, and 10% is shown in Figs. 4a–4d. At high concentrations the dominant reaction product is C_4H_{10} , but at low concentrations the C_4H_{10} product decreases and C_4H_8 dominates. At all concentrations, the PH_3 reaction product plateaus at a constant fraction of P_{TBP}^0 . The amount of H_2 produced (relative to P_{TBP}^0) increases for low input concentrations of TBP where the C_4H_8 reaction product dominates. The observed H_2 and HD concentrations in Fig. 4a ($P_{\text{TBP}}^0 = 0.2\%$) show significant scatter due to the low signal/noise ratio for low mass species at low concentrations.

Similar reaction products for the 5% concentration of TBP at high surface areas are shown in Fig. 5. The only significant difference between the reaction products at the low (Fig. 4c) and high (Fig. 5) surface areas is that the formation of H_2 begins at lower temperatures and reaches a higher value at the higher surface area, as discussed below.

No deuterated species were observed under any condition, except the small amount of HD formed at high temperatures. It appears that TBP decomposition is independent of the D_2 carrier gas. Another possible product, 2,2,3,3-tetramethylbutane (C_8H_{18}), monitored using the fragmentation peak at an m/e value of 99,¹³ was also absent, indicating that the butyl radical recombination reaction is unimportant.

DISCUSSION

The experimental evidence strongly suggests that a bimolecular reaction plays a significant role. A free radical process with the 4 major reactions 1–4 below is the simplest mechanism consistent with the data:



The $\text{C}_4\text{H}_9\text{—PH}_2$ bond is expected to be much weaker than the $\text{PH}_2\text{—H}$ bond,¹⁸ which causes the reduction in pyrolysis temperature for TBP relative to phosphine. Thus, the most likely pyrolysis mechanism is a radical process initiated by simple homolysis of TBP, reaction 1. Equation 2 is a hydrogen abstraction reaction confirmed by recent results which have shown that *tert*-butyl radicals, generated using azo-*t*-butane ($\text{H}_9\text{C}_4\text{N}=\text{NC}_4\text{H}_9$) at a concentration of 2.5%, can promote 45% decomposition of 5% TBP at a temperature as low as 300°C ¹⁹ (compared to the normal pyrolysis temperatures of approximately 475°C for TBP alone as seen in Fig. 3). The intermediate $\text{C}_4\text{H}_9\text{PH}$ produced from this reaction is unstable, and likely to further decompose

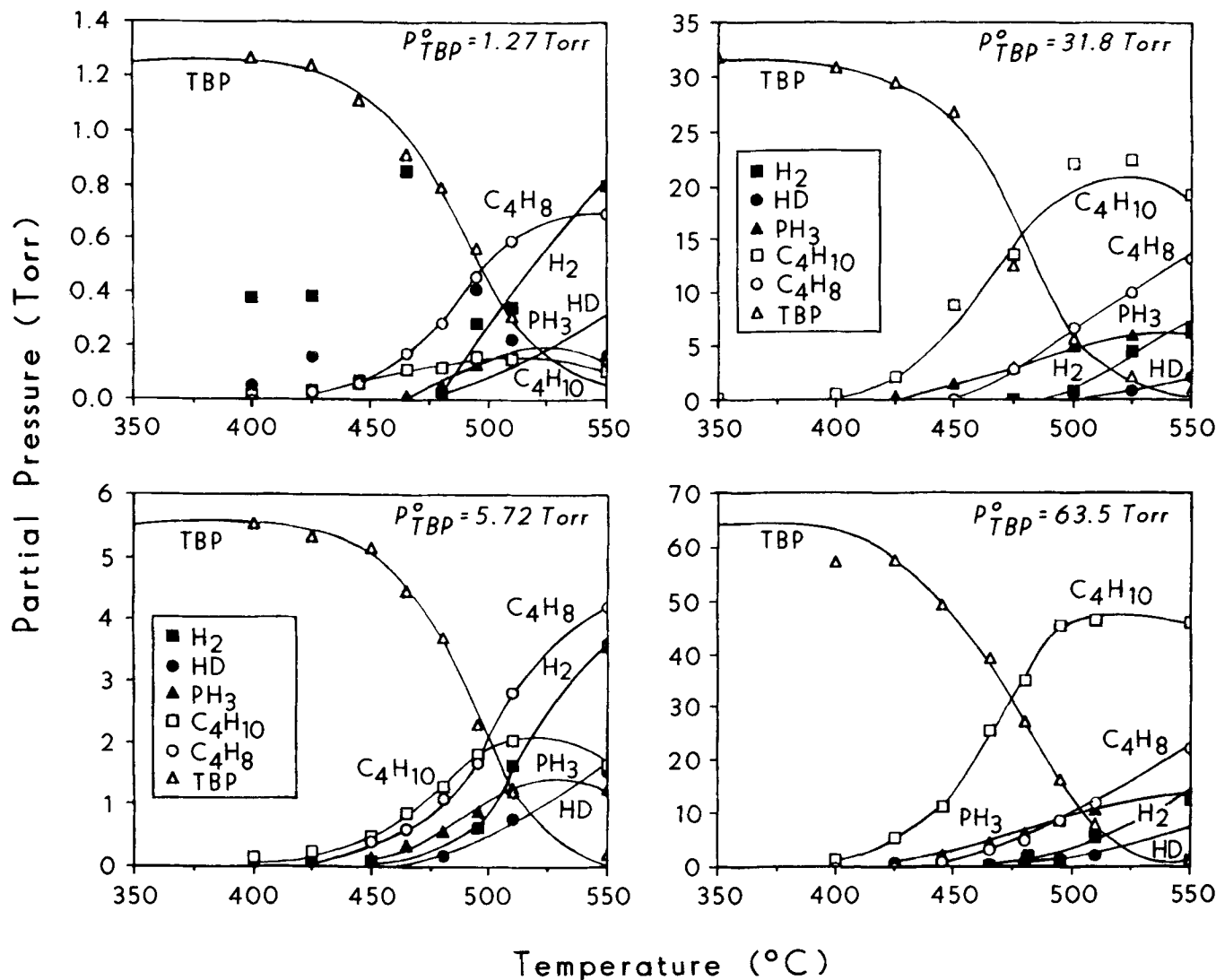


Fig. 4 — Products of TBP decomposition in an unpacked SiO₂ tube at various concentrations between 0.2 and 10%. The solid curves were drawn to fit the data.

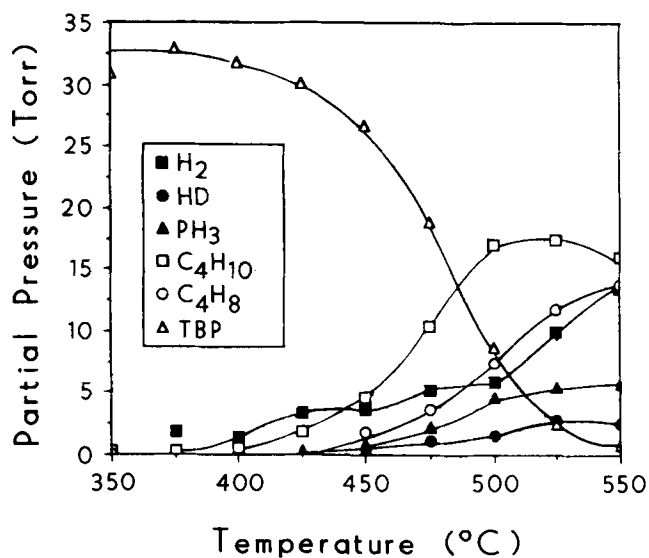


Fig. 5 — Products of TBP decomposition in a packed tube (SiO₂) at an input concentration of 5%.

via reaction 3. The 4th reaction is a *tert*-butyl radical removing step. Its rate constant parameters have been published.²⁰⁻²¹ This reaction has been postulated to play a role in the decomposition of C₈H₁₈.²²⁻²³ At 427–627° C the C₈H₁₈ molecule breaks into two *tert*-butyl radicals, while the predominant product observed was C₄H₈ indicating the importance of reaction 4.

The time derivatives of the partial pressures of TBP, C₄H₉PH, and C₄H₉ species can be written as,

$$dP_{\text{TBP}}/dt = -k_1 P_{\text{TBP}} - k_2 P_{\text{C}_4\text{H}_9} P_{\text{TBP}} \quad (5)$$

$$dP_{\text{C}_4\text{H}_9}/dt = k_1 P_{\text{TBP}} - k_2 P_{\text{C}_4\text{H}_9} P_{\text{TBP}} + k_3 P_{\text{C}_4\text{H}_9\text{PH}} - k_4 P_{\text{C}_4\text{H}_9} \quad (6)$$

$$dP_{\text{C}_4\text{H}_9\text{PH}}/dt = k_2 P_{\text{C}_4\text{H}_9} P_{\text{TBP}} - k_3 P_{\text{C}_4\text{H}_9\text{PH}} \quad (7)$$

Using the so-called steady state principle, *i.e.* assuming that the rate of formation of the intermediates can be considered to be equal to their rates

of disappearance,²⁴ allows the calculation of the partial pressures of the intermediates C₄H₉PH and C₄H₉, yielding

$$P_{C_4H_9PH} = k_1 k_2 / k_3 k_4 P_{TBP}^2 \quad (8)$$

$$P_{C_4H_9} = k_1 / k_4 P_{TBP}. \quad (9)$$

The validity of the steady state principle will be discussed below. Its use allows Eq. (5) to be expressed in an explicit and integrable form, *i.e.*

$$dP_{TBP}/dt = -k_1 P_{TBP} (1 + k_2/k_4 P_{TBP}). \quad (10)$$

The rate constant k_3 is absent in Eq. (10) because of the steady state approximation. This suggests that the rate of reaction 3 does not significantly affect the decomposition of TBP. Integration of Eq. (10) with the boundary condition $P_{TBP} = P_{TBP}^0$ at $t = 0$ yields²⁵

$$P_{TBP} = (k_1 P_{TBP}^0 e^{-k_1 t}) / [k_1 + k_1 k_2 / k_4 P_{TBP}^0 (1 - e^{-k_1 t})]. \quad (11)$$

The values of k_1 and $k_1 k_2 / k_4$ at each temperature can be determined by entering i) P_{TBP} , ii) P_{TBP}^0 and iii) the residence time, t , into the Eq. (11) for each case (refer to Figs. 4b–4d) to construct a simultaneous equation set, which is solved numerically. The results are displayed using an Arrhenius plot in Fig. 6. A linear regression analysis gives

$$\log k_1 (s^{-1}) = 17.5 - 63.09 (\text{kcal/mole}) / 2.303RT(K) \quad (12)$$

$$\log(k_1 k_2 / k_4) (l \text{ mol}^{-1} s^{-1}) = 12.7 - 36.70 (\text{kcal/mole}) / 2.303RT(K). \quad (13)$$

The rate constant k_2 can be determined since k_1 and k_4 are known.²⁰

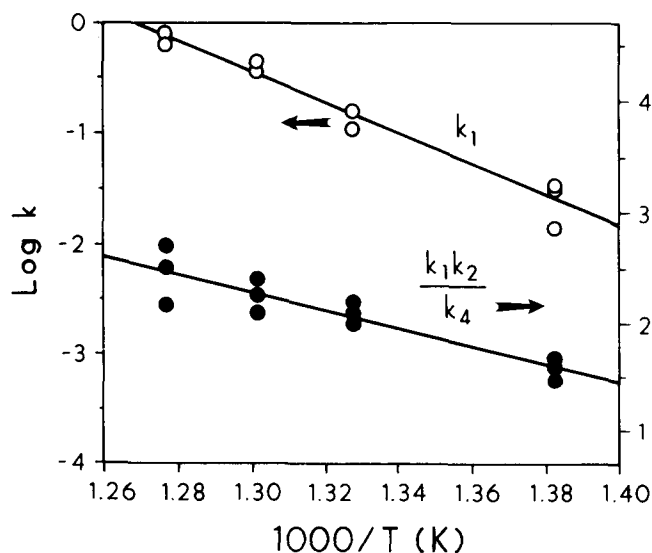


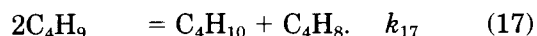
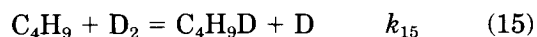
Fig. 6 — Arrhenius plots of k_1 and $k_1 k_2 / k_4$. At each temperature, there are 3 data for each curve since there are 3 equations with only two variables in each simultaneous equation set.

$$\log k_2 (l \text{ mol}^{-1} s^{-1}) = 11.8 - 17.23 (\text{kcal/mole}) / 2.303RT(K). \quad (14)$$

The A factor of the rate constant for the simple homolysis of TBP into two polyatomic groups (Eq. (12)) is $10^{17.5}$ which is similar to expected values of $10^{15} - 10^{17}$.²⁶ The activation energy of 63.09 kcal/mol for breaking the C₄H₉—PH₂ bond is quite reasonable. The difference between this value and that for PH₂—H (82.46 kcal/mol) is comparable to the bond strength difference between CH₃—H (104 kcal/mol) and CH₃—C₄H₉ (80 kcal/mol).^{18,27} The A factor for the abstraction reaction in Eq. (14) is higher than the expected value of $10^{8.5}$ for generic radical metathesis reactions,²⁶ so the estimated activation energy is also likely to be higher than expected. The higher empirical A factor obtained may result from either the scatter in the data in Fig. 6 or the higher A factor for k_4 used in the calculation.²⁰ The updated A factor for the rate constant k_4 is 1.6 orders of magnitude lower.²¹

At high input TBP concentrations, reaction 2 is much more important than reaction 4: the H radical concentration from reaction 4 is low. At low input TBP concentrations, reaction 4 becomes important, so the H radical concentration should be relatively higher. However, under these conditions, the concentrations of the parent TBP molecule and the intermediate species are quite low. Thus, an H radical chain reaction is considered unimportant. Nevertheless, the recombination of H radicals and the metathesis reaction between H radicals and the D₂ ambient are significant. This explains the relatively high concentrations of H₂ and HD found in low input TBP concentration experiments (see Figs. 4a–4b).

Other reactions for the removal of *tert*-butyl radicals should also be considered. Besides abstraction of H atoms from TBP molecules (reaction 2) and H elimination (reaction 4) there are three other available channels:



The rate constants for these reactions are listed in Table II.

Table II. Reaction Rate Constants

Reaction	logA	E*(kcal/mol)	Ref.
R1	17.5 ^a	63.09	Experimental
R2	11.8 ^b	17.23	Experimental
R3	17.5 ^a	54.83	Estimated
R4	16.3, ^a 14.7 ^a	43.6, 39.4	[20], [21]
R15	9.3 ^b	17.0	[28]
R16	9.0 ^b	—	[29]
R17	11.7 ^b	—	[20]

^as⁻¹.

^bl mol⁻¹s⁻¹.

COMPUTER MODELING

At 500° C and a TBP concentration of 0.9%, reaction 4 was calculated to be approximately 18 times faster than reaction 15, 2000 times faster than reaction 16, and 20 times faster than reaction 17. At a concentration of 10%, reaction 4 was still found to be approximately 18 times faster than reaction 15, and 200 times faster than reaction 16 but only 2 times faster than reaction 17. This is because reactions 4 and 15 are first order in the concentration of C_4H_9 , while reactions 16 and 17 are second order. For any concentration, reaction 17 is always approximately 100 times faster than reaction 16 since $k_{17}/k_{16} \approx 100$.²⁰ Although reaction 17 can be competitive with reaction 4 at higher input TBP concentrations, both are suppressed by reaction 2, based on Eq. 10.

This calculation explains the absence of C_8H_{18} and C_4H_9D in the experimental results. It also allows an estimate of the extent of reaction 17 which, unfortunately, could not be experimentally verified. The products of reaction 17 are indistinguishable from those of reactions 2 and 4. A forthcoming paper details the use of the deuterated TBP to help resolve this issue.¹¹

Computer modeling was based on reactions 1–4. The rate constant parameters for each reaction are given in Table II. The rate constant for reaction 3 is unknown, but is estimated to have the same A factor as for reaction 1 based on the similar geometries for both molecules, and to have an activation energy lower than for reaction 1 by 8.3 kcal/mol, the difference in bond energies between $HP-H$ (74.2 kcal/mol) and PH_2-H (82.46 kcal/mol).²⁷ The calculated results are shown in Figs. 7a–7d. The product curves mimic the general features of the experimental results: i) C_4H_{10} becomes a major product only at the higher concentrations, ii) the concentration of C_4H_8 shrinks at higher concentrations, and iii) TBP decomposition is enhanced by an increase in the input TBP concentration. By adjusting the Arrhenius parameters, the curves can be made to fit the data perfectly. However, this adds little to the analysis.

The validity of the steady state assumption is verified for the short-lived intermediates C_4H_9PH and C_4H_9 in Fig. 8. The concentrations are plotted

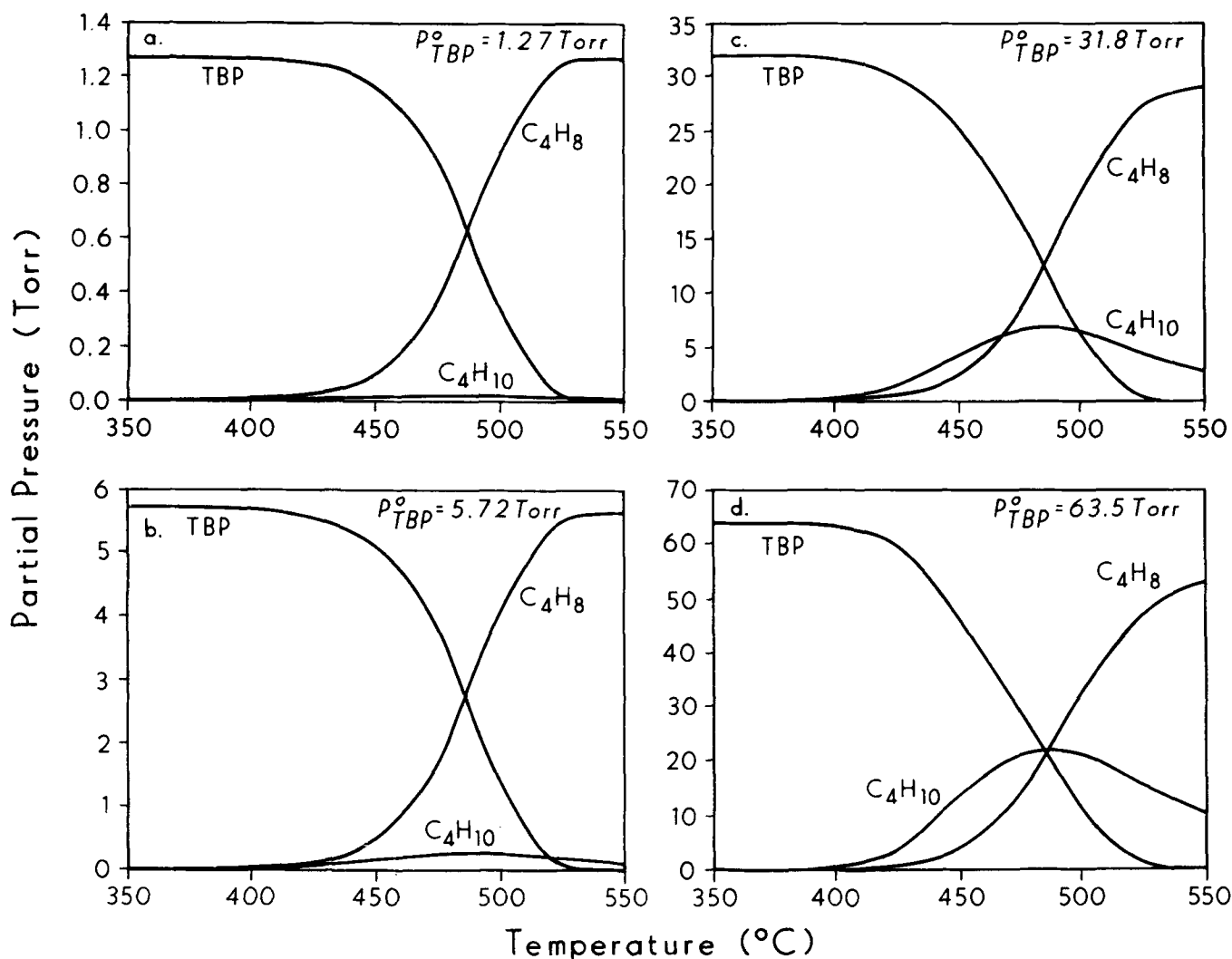


Fig. 7 — Computer modeling results of TBP, C_4H_8 , and C_4H_{10} partial pressures as a function of temperature for various initial TBP concentrations between 0.2% and 10%.

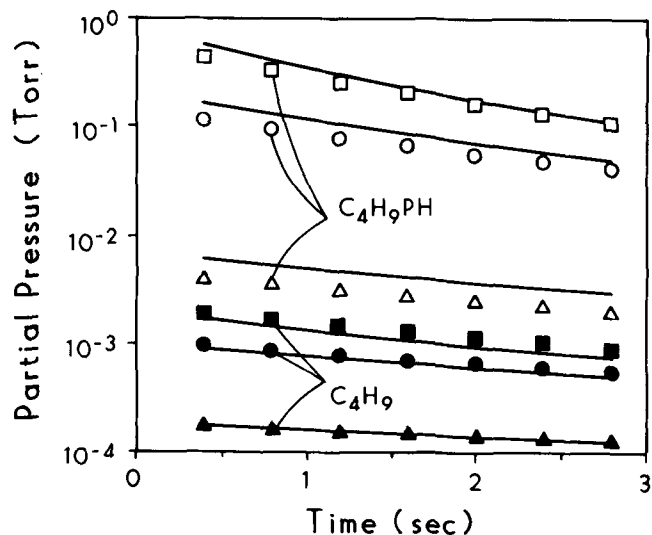
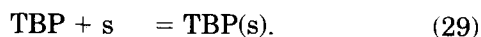
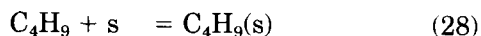
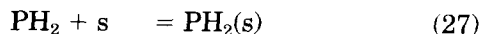
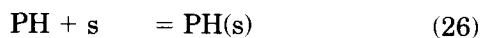
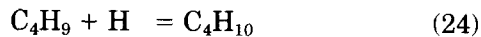
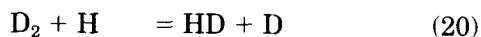
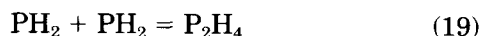
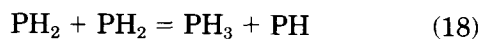


Fig. 8 — Comparison of numerical and analytical results for the C_4H_9PH and C_4H_9 partial pressures vs reaction time for various initial TBP concentrations of 10% (\square , \blacksquare), 5% (\circ , \bullet), and 0.9% (\triangle , \blacktriangle).

vs time, which is how long the flow has entered the reactor tube. At a constant flow the time indicates the position in the tube. The results obtained analytically using the steady state assumption (lines) were compared with those obtained numerically (symbols) using a time increment of $10 \mu s$. The temperature was $475^\circ C$ at which TBP pyrolysis is approximately 50% complete.

The real pyrolysis process is undoubtedly more complex than the simple mechanism proposed. Other reactions may include:



Such reactions could be used to explain the formation of PH_3 , H_2 , and HD . However, since there are no reliable rate constants for most of these reactions, quantitative analysis would be physically meaningless. Since no deuterated products were found in the experiments, the fate of most PH and PH_2 radicals is likely migration to the surface. Subsequent heterogeneous reactions occur to generate

H_2 and P_2 . Hydrogen was detected in the mass spectrum but P_2 is non-volatile, so it was condensed in the room temperature tube before entering the mass spectrometer. The enhanced H_2 formation with high surface areas illustrated in Fig. 5 can be explained as due to enhanced heterogeneous reactions between the PH and/or PH_2 species.

SUMMARY

The temperature and time dependence of TBP pyrolysis have been studied at input concentrations between 0.2 and 10% in a D_2 ambient with various SiO_2 surface areas. The results show that an SiO_2 surface does not significantly influence TBP pyrolysis. However, the pyrolysis rate and products are strongly dependent on the input TBP concentration. The results are explained using a simple chain reaction mechanism involving: i) homolytic scission of TBP to form C_4H_9 radicals, ii) C_4H_9 radical attack of TBP by hydrogen abstraction forming C_4H_{10} and C_4H_9PH , iii) decomposition of C_4H_9PH , and iv) a removing reaction to deplete the C_4H_9 radicals. Arrhenius parameters for these reactions were determined.

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REFERENCES

- G. B. Stringfellow, *Semiconductors and Semimetals* 22A, 209 (1985).
- S. M. Sze, *Physics of Semiconductor Devices*, 2nd edition (John Wiley and Sons, N.Y., 1981).
- G. B. Stringfellow, *J. Cryst. Growth* 70, 133 (1984).
- G. B. Stringfellow, *J. Electron. Mater.* 17, 327 (1988).
- T. F. Kuech and E. Veuhoff, *J. Cryst. Growth* 68, 148 (1984).
- C. H. Chen, C. A. Larsen, G. B. Stringfellow, D. W. Brown and A. J. Robertson, *J. Cryst. Growth* 77, 11 (1986).
- C. H. Chen, C. A. Larsen, G. B. Stringfellow, *Inst. Phys. Conf. Ser.*, No. 83, 75 (1987).
- R. R. Saxena, J. E. Fouquet, V. M. Sardi, and R. L. Moon, *Appl. Phys. Lett.* 53, 304 (1988).
- N. I. Sax, *Dangerous Properties of Industrial Materials*, (VanNostrand Reinhold, N.Y., 1979)
- S. H. Li, N. I. Buchan, C. A. Larsen, and G. B. Stringfellow, *J. Cryst. Growth*, to be published.
- S. H. Li, N. I. Buchan, C. A. Larsen, G. B. Stringfellow, W. P. Kosar, and D. W. Brown, *J. Appl. Phys.*, to be published.
- N. I. Buchan, C. A. Larsen and G. B. Stringfellow, *Appl. Phys. Lett.* 51, 28 (1987).
- B. Boyd, (Editor), *Selected Mass Spectral Data (Standard)*, (Thermodynamics Research Center, The Texas A&M University System, College Station, Texas, 1983) Series No. 56, 70, 114, 1219.
- J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.* 78, 546 (1956).
- O. Levenspiel, *Chemical Reaction Engineering*, 2nd edition, (John Wiley and Sons, N.Y., 1972) pp. 1-86.

16. G. G. Devyatykh, V. M. Kedyarkin and A. D. Zorin, *Russ. J. Inorg. Chem.* **14**, 1055 (1969).
17. C. A. Larsen, N. I. Buchan and G. B. Stringfellow, *J. Cryst. Growth* **85**, 148 (1987).
18. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 3rd Edition, (Allyn and Bacon, Inc., Boston, 1973) pp. 177-224.
19. S. H. Li, N. I. Buchan, C. A. Larsen, and G. B. Stringfellow, *J. Cryst. Growth*, to be published.
20. V. N. Kondratiev, *Rate Constants of Gas Phase Reactions*, (National Bureau of Standards, U.S. Depart. of Commerce, Washington, D.C., 1972) pp. 176-178.
21. C. E. Canosa and R. M. Marshall, *Int. J. Chem. Kinetics* **13**, 303 (1981).
22. J. E. Taylor and T. S. Milazzo, *Int. J. Chem. Kinetics* **10**, 1245 (1978).
23. J. A. Walker and W. Tsang, *Int. J. Chem. Kinetics* **11**, 867 (1979).
24. S. H. Maron, and J. B. Landon, *Fundamentals of Physical Chemistry*, Macmillan Publishing Co. Inc., N.Y. (1976) pp. 673-719.
25. K. B. Yerrick and M. E. Russell, *J. Phys. Chem.* **68**, 3852, (1964).
26. S. W. Benson, *Thermodynamical Kinetics*, (Wiley-Interscience, N.Y., 1979) p. 97, and p. 156.
27. J. Berkowitz, L. A. Curtiss, S. T. Gibson, J. P. Greene, G. L. Hillhouse and J. A. Pople, *J. Chem. Phys.* **84**, 375 (1986).
28. G. A. Evans and R. W. Walker, *J. Chem. Soc. Far. Trans. 1*, **75**, 1458 (1979).
29. W. C. Gardiner, Jr. (Editor), *Combustion Chemistry*, Springer-Verlag, N.Y., 1984) p. 344.