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An empirical study of the effect of the variables in a flash vacuum pyrolysis (FVP) experiment

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The effect of the variation of the experimental parameters on the conversion of precursor to products in a typical flash vacuum pyrolysis (FVP) experiment was investigated empirically. Temperature-conversion plots can be used to optimise FVP conditions and their mechanistic significance is exemplified. At a given temperature, the conversion can be increased by an increase in the background pressure, or by packing a section of the furnace tube with inert material (particularly when placed at the trap end of the furnace tube) or by employing a catalyst. Despite the prevailing view that only intramolecular reactions take place by FVP, it has been shown by a 'dual-FVP' cross-over experiment that the dimerisation of benzyl radicals occurs in the gas-phase, before the cold trap, under standard conditions. However, reduction in through-put rate, increase in furnace temperature and reduction in background pressure all reduce the amount of gas-phase coupling.

The technique of flash vacuum pyrolysis (FVP) experimentally involves the vacuum sublimation or distillation of a substrate through a hot tube (generally at temperatures between 300–1000 °C) to induce chemical change. After passing through the tube, the products are quenched at low temperatures in a trap placed at the exit point of the furnace tube.[1,2] The pyrolysis is usually considered to take place under dilute, short contact time conditions in the gas phase such that individual molecules react intramolecularly in the effective absence of other molecules of substrate, products or substantial amounts of oxygen. The technique therefore produces much cleaner results than other forms of pyrolysis. FVP is a robust, highly reproducible method and has found widespread use in applications ranging from matrix isolation and mechanistic studies to preparative organic chemistry.[3]

As is the case with any method which depends on gas flow, the residence time of substrate molecules in the hot (reacting) zone is a key parameter,[1] and this in turn depends on a number of variables including the pressure and temperature, the dimensions of the reactor tube, throughput rate and the presence of (inert) packing material (if any).[1] However, in any one laboratory where the furnace dimensions, temperature gradient and packing are fixed and the vacuum system delivers a fairly constant pressure, the main variables are likely to be throughput rate and furnace temperature. It should be noted that atmospheric pressure flow pyrolysis (carried out by injecting the substrate into a gas stream at the top of a vertical heated tube), has many more variables in practice, including choice of solvent (if any) and carrier gas, nature of preheater (if any), heat exchange medium and mode of product trapping.

Although FVP experiments are highly reproducible using one set of apparatus (see below), the variables are often not specified in literature reports of FVP applications, so it can be difficult to reproduce such conditions in another laboratory without carrying out a series of trial experiments. In the work described here, we have therefore systematically varied the FVP parameters and monitored the effect on conversion to products to provide empirical guidelines on their relative importance and on the design of the preparative FVP experiment. In all the experiments, the substrate was distilled through a horizontal silica tube (overall dimensions 35 × 2.5 cm) heated by an electrical tube furnace. The temperature was measured at the centre of the furnace; it is relatively constant for much of the central region of the tube but becomes cooler towards the ends, in particular the open (trap) end. The product trap (U-tube) was situated at the exit point of the furnace and the pressure was recorded between the product trap and a high capacity rotary oil pump (Fig. 1).

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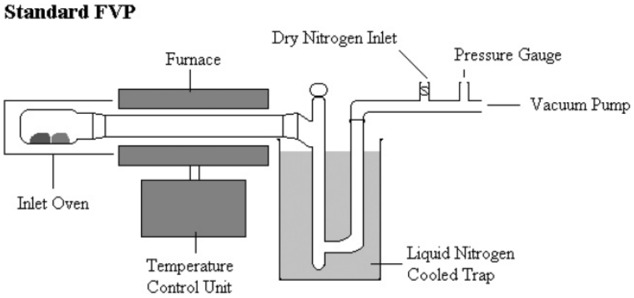
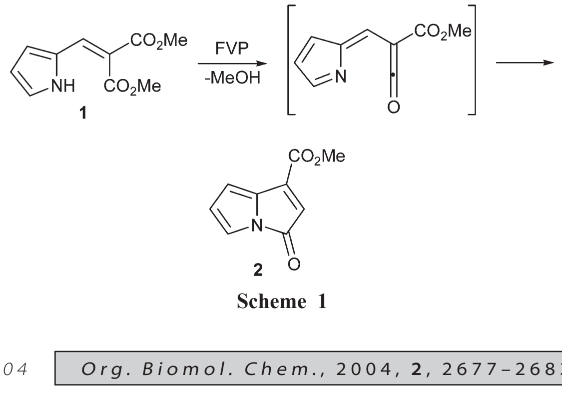


Fig. 1 FVP apparatus.

1. Effect of furnace temperature: temperature–conversion plots

Furnace temperature is intuitively the most important variable in an FVP experiment. As a model reaction, the temperature dependence of the cyclisation of the malonate **1** to the 3-oxopyrrolizine carboxylic ester **2** (Scheme 1) was studied.[4] This reaction was chosen because it takes place over a typical FVP temperature range [100% conversion at 650 °C (0.01 mbar) using an empty furnace tube] and its sensitivity to experimental variables is readily monitored because a temperature range of some 150 °C is required to increase the conversion from 10% to 90%. In addition, there are no significant side-reactions. The variation of substrate conversion with temperature (Table 1, entries 1–5) follows a sigmoid curve (Fig. 2) reflecting the Boltzmann distribution of molecules in the tube. Thus at low temperatures only a few molecules possess enough energy to react. At higher temperatures the steep region of the curve reflects the greater number of molecules in the central region of the Boltzmann distribution. At the highest temperatures the curve again flattens out since only a few molecules do not possess enough energy to react.



Scheme 1

Table 1 FVP of **1** to give **2** under a variety of FVP conditions

Entry	Quantity/mg	T_i/°C[a]	T_f/°C[b]	P/mbar[c]	Time/min[d]	Packing	% Product	Notes
1	30	120	450	0.01	5	none	9.3	
2	32	120	500	0.01	5	none	44	
3	31	120	550	0.01	5	none	72	
4	30	120	600	0.01	5	none	95	
5	32	120	650	0.01	5	none	100	
6	30	120	500	0.01	5	none	44	1
7	25	120	500	0.1	6	none	90	
8	30	120	500	1	15	none	100	2
9	30	80	500	0.005	4	none	41	
10	30	120	500	0.005	5	none	43	1
11	25	200	500	0.005	5	none	32	
12	29	120	400	0.005	7	SiO_2[e]	0	3
13	36	120	450	0.01	5	SiO_2[e]	9.5	3
14	30	120	475	0.01	5	SiO_2[e]	78	3
15	32	120	500	0.01	7	SiO_2[e]	100	3
16	31	120	450	0.01	5	SiO_2[e]	15	4
17	31	120	450	0.01	5	SiO_2[e]	5	5
18	32	120	450	0.01	5	SiO_2[f]	31	3
19	26	120	450	0.01	4	SiO_2[f]	80	4
20	28	120	450	0.005	5	SiO_2[f]	7	5
21	26	120	450	0.01	15	SiO_2[f]	99	6
22	26	120	450	0.01	5	por[g]	39	3
23	28	120	450	0.01	4	por[g]	46	4
24	26	120	450	0.01	5	por[g]	23	5
25	32	120	450	0.01	3	por[g]	79	
26	31	120	300	0.01	5	SiO_2[h]	48	4
27	32	120	350	0.01	5	SiO_2[h]	79	4
28	29	120	450	0.01	5	SiO_2[h]	100	4

[a] Inlet temperature. [b] Furnace temperature. [c] Background pressure (measured after the product trap). [d] Time required for complete distillation of the substrate through the furnace (unless otherwise stated). [e] A stack of eight SiO_2 tubes (5 × 0.6 cm) was placed in the furnace. [f] Sections of the furnace were packed throughout the tube diameter with portions of silica wool (typically 5 cm length within the furnace tube, *ca.* 1.3 g silica wool). For entry 21, the whole length of the tube was packed with silica wool. [g] Sections of the furnace were packed throughout the tube diameter with porcelain chips [typically 20 g, held in place by a small amount of silica wool (3–4 cm)]. For entry 25, the whole length of the tube was packed with porcelain chips. [h] Eight silica tubes (5 × 0.6 cm) were coated with TLC grade silica gel, as follows.[14] Methanol (40 cm^3) was added to silica gel (20 g) to produce a thick slurry. The silica tubes were dipped in the slurry until thoroughly coated. Excess coating was removed from the outside of the tubes, which were then dried at 120 °C for 4 h before being stacked in the furnace (trap end).

Notes: 1. Repeat of entry 2. 2. Only small amount of pyrolysate recovered from product trap. 3. Packing located in the centre of the furnace. 4. Packing located at the trap end of the furnace. 5. Packing located at the inlet end of the furnace. 6. The whole length of the tube was packed with silica wool.

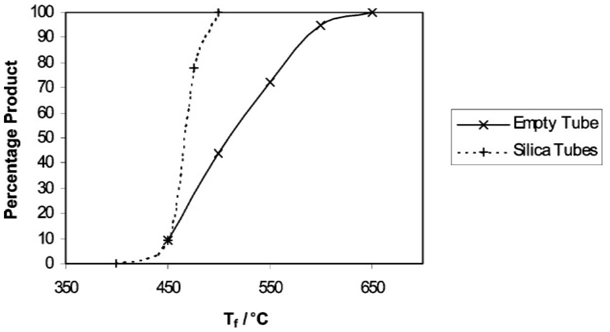


Fig. 2 Temperature–conversion plot for **1**→**2** using an empty furnace tube and using a furnace tube containing a central packing of silica tubes.

The results shown in Table 1, entries 2, 6 and 10, demonstrate the reproducibility of a typical FVP experiment (44 ± 1% conversion), even at a point in the sigmoid curve where there is a relatively steep temperature dependence.

Temperature–conversion plots have been used in the past to identify the optimum pyrolysis temperature[5,6] and to monitor the progress of consecutive reactions.[7] However, the position and shape of the sigmoid curve with respect to the temperature axis is related in principle to the activation energy of the process and therefore contains additional mechanistic information. As an illustration of how this can be used in practice, we have reinvestigated the pyrolyses of the hydrazones **3**[8] and **4**[9] and the related vinamidine **5**.[10] Hydrazones such as **3** are known to cyclise by a free radical mechanism[8] because of the observed formation of rearranged products *via* a spirodienyl intermediate (Scheme 2). In contrast, vinamidines such as **5** are known to cyclise by a concerted electrocyclisation-with-elimination process in which a 1,5-sigmatropic hydrogen atom shift takes place as a key step at an intermediate stage which is not observed in radical processes (Scheme 2).[10] However, there is no substantive evidence to support the radical cyclisation mechanism for the hydrazone **4**, since in substituted examples, the spirodienyl radical **6**, if formed, is transformed to products exclusively by C–N bond migration (Scheme 2).[9] Because a number of products are formed in these reactions, the amount of remaining starting materials **3**, **4** and **5** at various furnace temperatures is shown on the graph (Fig. 3) and in Table 2. As can be seen from the data, conversion of the hydrazones **3** and **4** to products begins below 500 °C and both show similar, steep, temperature dependence. In contrast, the vinamidine **5** is stable at above 600 °C and a greater temperature range is required for complete conversion to products. Hence the similarity in mechanism for the reactions of **3** and **4** is confirmed, which establishes that the cyclisation of **4** almost certainly proceeds *via* an iminyl radical intermediate rather than by a concerted mechanism.

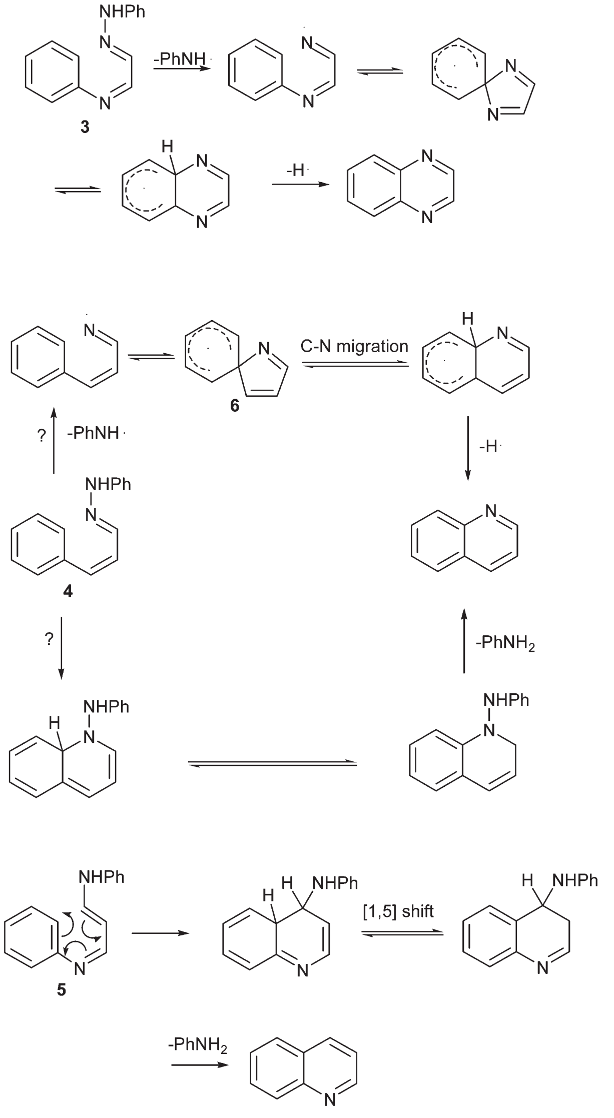
2. Effect of pressure variation

The background pressure in the system was easily varied by 2 orders of magnitude by introduction of nitrogen gas *via* a needle valve located between the product trap and the pumps. An increase in pressure is expected to increase the contact time because of a reduced pressure gradient between inlet and trap. Indeed, at 500 °C the 45% conversion of **1** to **2** at 10^{-2} mbar is increased to 90% at 10^{-1} mbar and is almost quantitative at 1 mbar (Table 1, entries 6–8). These results show that conversion is strongly dependent on the pressure in the system. It is therefore important that the pressure is kept constant for each run used for the construction of temperature–conversion plots. In practice this is not usually a problem since, in the absence of leaks in the vacuum line, the pump usually delivers a steady pressure. However, if a gas is generated in the FVP

Table 2 FVP of **3**–**5** at various temperatures

Precursor	Quantity/mg	T_i/°C[a]	T_f/°C[b]	P/mbar[c]	Time/min[d]	% precursor[e]
3	25	120	475	0.007	35	78
3	25	120	500	0.007	35	64
3	25	120	550	0.007	35	17
3	25	120	575	0.007	35	6
3	25	120	600	0.007	35	5
3	25	120	650	0.007	35	5
4	35	150	450	0.01	25	77
4	35	150	500	0.01	25	16
4	35	150	550	0.01	25	0
4	35	150	600	0.01	25	0
5	25	100	650	0.014	20	89
5	25	100	700	0.014	20	60
5	25	100	750	0.014	20	30
5	25	100	800	0.014	20	9
5	25	100	850	0.014	20	3

[a] Inlet temperature. [b] Furnace temperature. [c] Background pressure (measured after the product trap). [d] Time required for complete volatilisation of the substrate through the furnace (unless otherwise stated). [e] See Experimental section for explanation.



Scheme 2

reaction, which contributes to the background pressure (*e.g.* N_2 or CO), substantially increased contact times should be anticipated. This is likely to be particularly important when a reaction is scaled up, since the inevitable increase in throughput rate will contribute to an even greater increase in background pressure (see below).

It should be noted that in some highly exothermic reactions such as those involving carbenes or nitrenes, intermediates may be generated in vibrationally excited states which may be deactivated by collisions. Under these conditions of 'chemical activation',[11] the excess energy may be dissipated by collision *i.e.* subsequent secondary reactions may be minimised by performing the reaction in the presence of a carrier gas.

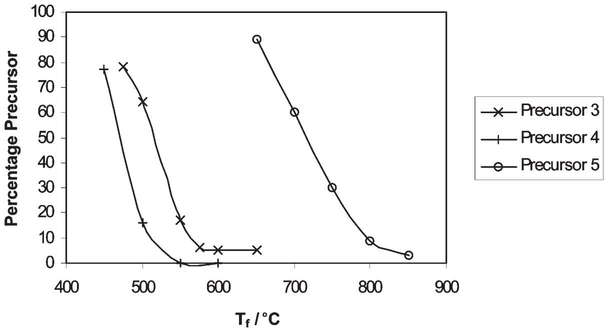


Fig. 3 Temperature–conversion plot for the pyrolyses of **3**–**5**, showing remaining starting materials.

FVP reactions can be carried out at a lower pressure, *e.g.* by use of an oil diffusion pump in series with the rotary pump. In our experience there is little advantage in using these conditions for preparative reactions, except where the substrate is poorly volatile.

3. Effect of substrate throughput rate

The throughput rate is governed by the volatilisation temperature of the substrate from the inlet. Variation of inlet temperature from 80–200 °C has relatively little effect on the conversion of the model precursor **1** (Table 1, entries 9–11; 38 ± 6% at 500 °C). This parameter is therefore not especially critical (in the absence of evolved gases—see above) and can be varied to give a convenient throughput rate with relatively little effect on contact time and conversion to products (though see Section 6 below). This result explains the high reproducibility of FVP experiments; at constant pressure and with an empty furnace tube, the furnace temperature becomes effectively the only experimental variable. On the negative side, if an FVP reaction cannot be optimised by control of furnace temperature then there is little scope for further optimisation unless furnace packings or catalysts (see below) can be introduced to the hot tube.

4. Effect of furnace packing materials

It is well known that packing a section of the furnace tube with an 'inert' material (such as silica chips) can result in a reduction of furnace temperature required for a conversion by *ca.* 50–100 °C.[12] However, as pointed out by Brown[12] it is not clear whether this is due to contact time effects or to some specific surface effect of the so-called 'inert' packing. We have therefore studied the effects of various packing materials located at different parts of the furnace tube. Thus, if some specific surface phenomenon is involved, the effect should be greatest when the packing is located at the centre of the tube—*i.e.* where the temperature is greatest. Three common packing materials were studied for their effect on the **1**→**2** conversion, *viz.* silica tubes, silica wool and porcelain chips and in all cases the whole section of the tube was packed.

As shown in Fig. 2, (and Table 1, entries 12–17) the major effect of packing the centre of the furnace tube longitudinally with small silica tubes (stack of 8 tubes, each 5 × 0.6 cm) is to narrow the temperature range of the conversion. Thus a temperature increase of only *ca.* 50 °C is required to increase the conversion from 10% to >90% (*c.f.* the 150 °C range required in the absence of the packing). This implies that the packing has the effect of equalising the energies of the precursor molecules (*i.e.* the half-height width of the Boltzmann distribution is reduced). This may be due to disruption of the flow in the centre of the tube so that all the molecules experience a similar (increased) number of surface collisions. Although the temperature of onset of reaction is not significantly affected by this packing, complete conversion to products is observed at 500 °C rather than at 650 °C in the absence of the packing. These results suggest that such packing might be used to minimise the effect of secondary, subsequent pyrolysis processes on an initial reaction. At low conversions, the position of the packing in the tube has relatively little influence (Table 1 entries 13, 16 and 17), though it appears that the major effect is *not* found when the packing is located at the centre of the furnace tube.

This trend was even more apparent when silica wool (1.3 g, spread along a *ca.* 5 cm length of tube) was used as the packing material (Table 1, entries 18–21 and Fig. 4). For these experiments, full temperature–conversion plots were not carried out, but the effects of various packing configurations on the conversions at 450 °C were monitored. The silica wool has a much larger surface area than the tubes, but if a surface reaction is involved, the effect would be expected to be greatest where the surface is hottest—*i.e.* when the wool is placed in the centre of the tube. In the event, the conversion from **1** to **2** at 450 °C was increased from 7–9% (in the absence of packing, or with packing at the inlet end of the furnace tube) to 31% (with packing in the centre of the tube) but was further increased to 80% when the packing was placed at the trap end of the furnace tube. It is clear from these results that (i) silica wool has a greater effect on the conversion than silica tubes; (ii) an increase in the number of molecular collisions at the inlet end of the tube (*i.e.* in a pre-heating zone) has little influence on the conversion; (iii) the major effect is seen when the packing is at the trap end and not when it is in the centre of the furnace tube. This suggests that there is no 'surface' phenomenon involved with 'inert' packing materials such as silica, and instead the major influence must be a reduction in flow rate causing an increase in contact time. The effect of this increase in contact time is greatest when the molecules are forced to spend this period in the hottest zone of the furnace.

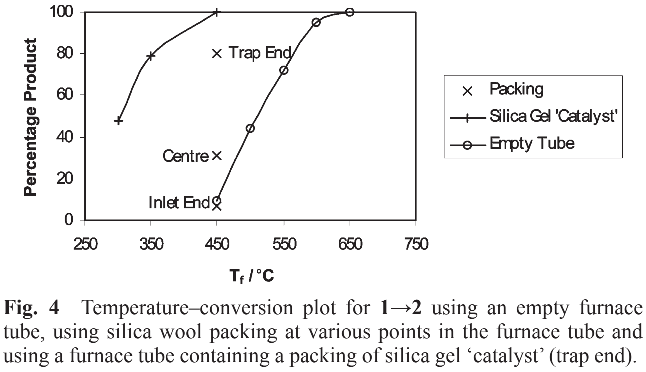


Fig. 4 Temperature–conversion plot for **1**→**2** using an empty furnace tube, using silica wool packing at various points in the furnace tube and using a furnace tube containing a packing of silica gel 'catalyst' (trap end).

In one experiment in which the whole furnace tube was packed with silica wool (Table 1, entry 21), the packing proved to be too dense for effective gaseous flow through the furnace and only a small amount of product (with high conversion) was obtained.

Broadly similar results were obtained when porcelain chips (20 g, filling a *ca.* 5 cm segment of the furnace tube, held in place with silica wool) were used as the packing material (Table 1, entries 22–25; 450 °C pyrolysis temperature; 7–9% conversion in the absence of packing). Again the effect was greatest when the packing was at the trap end of the furnace tube (46% conversion) but there was rather less distinction compared with the run in which the packing was placed in the centre of the tube (39% conversion). In this case packing at inlet end of furnace tube increased the conversion significantly (to 23%) which suggests that the porcelain may be a more efficient 'pre-heater' than the silica used in the previous experiments.

These results show that relatively short sections of inert packing material within the furnace tube of an FVP experiment can dramatically influence the conversion to products, particularly when the packing is located away from the centre of the tube at the trap end of the furnace. In the first place, the furnace temperature can be reduced, but because the major effect seems to be an increase in the contact time, this does not mean that 'milder' conditions are experienced by substrate molecules. Perhaps more important, the reduction in the temperature range required for complete conversion to products may give the opportunity for much finer control, particularly if two or more successive thermal processes can take place.

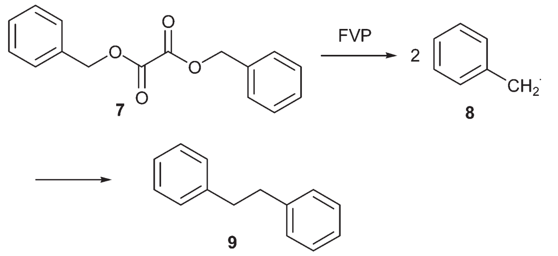
5. Effect of 'catalysts' in the furnace

Surprisingly little systematic work has been carried out on the use of solid-phase catalysts in the short contact time gas-phase FVP experiment,[13] though solid-phase reagents have been employed in the VGSR (Vacuum Gas-Solid Reaction) technique.[2] In one interesting application, Storr and co-workers used silica tubes coated with TLC-grade silica-gel, and observed substantial reduction in furnace temperatures for dehydration and related reactions.[14] The model reaction **1**→**2** involves consecutive elimination, (thought to be *via* an intramolecular concerted process) and electrocyclisation and it is not clear that surface catalysis should accelerate either step of this process. In the event, a very significant effect was observed when Storr's conditions were used [Table 1, entries 26–28, (silica tubes at trap end of furnace) and Fig. 4] such that the temperature for complete conversion was reduced to 400 °C, some 250 °C lower than with an empty tube. In this set of experiments, the steep temperature dependence found for silica tubes centrally located in the furnace was not found (Fig. 2), but it is anticipated that a greater effect may be observed if the 'catalyst' is placed in the hottest (centre) zone of the furnace tube. It is clear that a more systematic study of catalytic conditions may provide an added dimension to the FVP experiment and significantly increase the utility of the method in synthesis. Further examples will be reported in future publications.

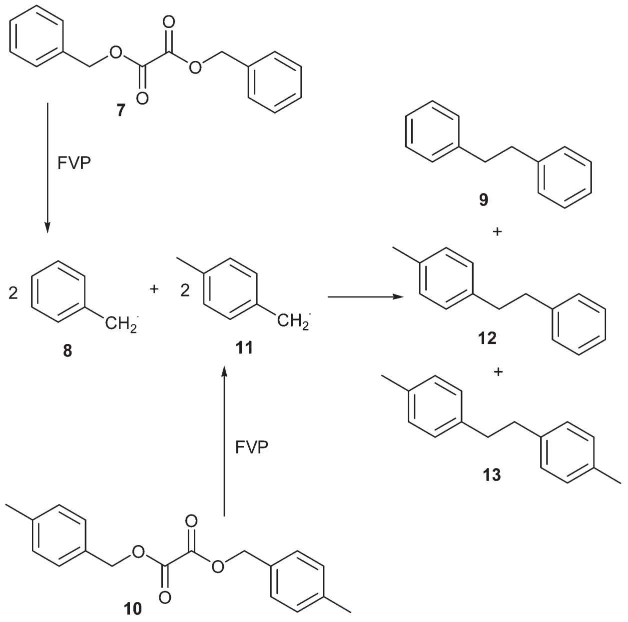
6. Intermolecular reactions—the coupling of benzyl radicals

FVP reactions are dominated by intramolecular processes. Of the few intermolecular reactions which are preparatively useful, most are dimerisations of reactive species such as carbenes or radicals. Yet not all radicals dimerise. Phenyl radicals generally undergo hydrogen atom capture whereas benzyl radicals couple to give excellent yields of bibenzyls.[15] It was therefore of interest to understand the mechanism of such dimerisations more precisely and in particular to define the region(s) of furnace and trap where the actual coupling reaction takes place. In very early work, Hedaya and McNeil have shown that the level of the cross-coupling reaction of cyclopentadienyl and allyl radicals could be reduced by locating the trap at a greater distance from the furnace exit, which suggests that—in their system—the coupling reaction takes place in the cold trap under standard conditions.[16] In addition, benzyl radicals (generated by FVP of benzyl bromide) can survive as far as a neon matrix where they can be detected by EPR spectroscopy.[17] However, the apparatus used for these experiments may be very different from that in use today for 'preparative' FVP experiments.

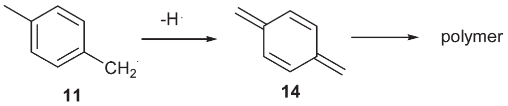
The dimerisation of benzyl radicals **8**, generated by pyrolysis of oxalate esters[18] (*e.g.* **7**) (Scheme 3) to give bibenzyl **9** was therefore chosen as the model. A control experiment, in which dibenzyl oxalate **7** and di-*p*-tolyl oxalate **10** were cosublimed from the same inlet tube through the same furnace tube at 800 °C, gave bibenzyl **9**, 4-methylbibenzyl **12** and 4,4′-dimethylbibenzyl **13** (Scheme 4). The products are readily identified by the characteristic chemical shift of the methylene protons in the ^{1}H NMR spectrum at δ_H 2.93, 2.90 and 2.87 respectively.[19] The ratio of these products **9** : **12** : **13** was 46 : 36 : 18. There is clearly a much greater level of bibenzyl **9** than 4,4′-dimethylbibenzyl **13**. This is due to an alternative reaction of the 4-methylbenzyl radical **11**, which can lose a hydrogen atom to generate *p*-xylylene **14** which polymerises (Scheme 5).[20] The maximum amount of cross-over product **12** is therefore controlled by the available amount of 4-methylbenzyl radical **11**. Indeed the relative amounts **12** and **13** (36 : 18) are in a 2 : 1 ratio which confirms that the reaction takes place in intermolecular fashion *via* benzyl radicals and not by an intramolecular collapse of the oxalate.



Scheme 3



Scheme 4



Scheme 5

In order to identify where the dimerisation takes place, a second cross-over experiment was designed as follows. Two FVP inlets and furnace systems were set up with the effluent from both furnaces collected in a single trap, which was itself connected to the standard vacuum line (Fig. 5). The distance between the exit point of each furnace and the liquid nitrogen level in the trap was *ca.* 8 cm. Dibenzyl oxalate **7** was sublimed through furnace 1 (generally 800 °C) and di-*p*-tolyl oxalate **10** was sublimed through furnace 2 (same temperature as furnace 1) at comparable rates, and the pyrolysate (consisting of bibenzyls and some insoluble *p*-xylylene polymer) was analysed by ^{1}H NMR spectroscopy. The results under a variety of conditions are shown in Table 3. Under standard conditions with a moderate throughput rate (100 min per mmol of substrate), little cross-over product is obtained based on the ratio of **12** : **13** (Table 3, entry 1). Under these conditions, therefore, pressures are high enough for *ca.* 94% of the product-forming events to take place in the gas-phase (or at the surface of the furnace tube) before the effluent reaches the liquid nitrogen trap. If the throughput rate is reduced (by lowering the inlet temperature) the amount of cross-over product is increased and so a larger proportion of the benzyl radicals **8** and **11** has sufficient lifetime to survive to the vicinity of the trap (Table 3, entries 1–6 and Fig. 6). This corresponds to an increased proportion of the radical coupling reaction taking place in the cold trap rather than in the gas-phase. Entries 3 and 4 in Table 3 demonstrate the reproducibility of the results. The sigmoidal nature of the relationship (Fig. 6) suggests that under these standard FVP conditions the ratio of cross-over product can never reach the statistical 67 : 33 value required for all the coupling events to take place after mixing of the gas streams. As with the temperature-conversion graphs discussed earlier, this sigmoidal behaviour reflects the Boltzmann energy distribution of species generated by FVP.

The level of cross-over product is also increased if the system pressure is reduced (compare Table 3, entries 2 and 8) though the effect is relatively small. An increase in the temperature of the furnaces also results in a reduction in gas-phase dimerisation; presumably the radicals have a longer mean free path under these conditions (Table 3 entries 1 and 7). An increase in *p*-xylylene polymer was also noted at this temperature. Taken together, these results show that subtle gradation in the timing of product forming events can be induced in FVP experiments, even by simple variation of the substrate throughput rate. The results of these ‘dual-FVP’ experiments also have implications in other intermolecular FVP reactions, such as the trapping of a reactive intermediate by an external agent. In these experiments it is generally more convenient to add the trapping agent to the cold trap rather than to carry out the pyrolysis in the presence of a gas-phase stream of the trapping agent. Hence the amount of intermediate which survives to the trap can be maximised by reduction in pressure, reduction in through-put rate and increase in furnace temperature.

7. Conclusions

In conclusion, it is hoped that the work described in this paper will provide a more rational basis for the design and interpretation of

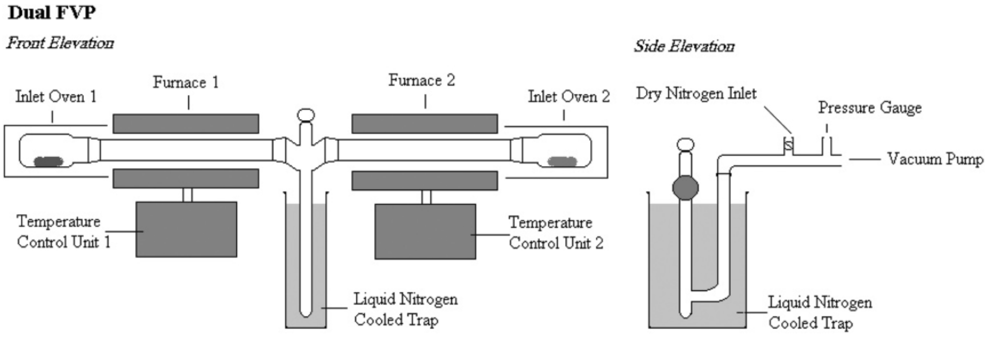


Fig. 5 ‘Dual FVP’ apparatus.

Table 3 'Dual- FVP' of the oxalates **6** and **7** under various conditions[a,b]

Entry	T_f/°C[c]	Time/min[d]	P/mbar[e]	Ratio of **11** : **12**
1	800	21	0.01	6 : 94
2	800	55	0.01	19 : 81
3	800	60	0.01	30 : 70
4	800	61	0.01	29 : 71
5	800	86	0.01	40 : 60
6	800	101	0.01	47 : 53
7	950	15	0.01	25 : 75
8	800	50	10^{-5}[f]	25 : 75

[a] Samples of **6** and **7** (both 0.2 mmol) were used in each case. [b] Inlet temperatures adjusted to provide control of pyrolysis time. [c] Furnace temperature. [d] Time measured from the first appearance of product in the trap until volatilisation of the precursors has been completed. [e] Background pressure (measured after the product trap); high capacity rotary pump unless otherwise stated. [f] Oil diffusion pump.

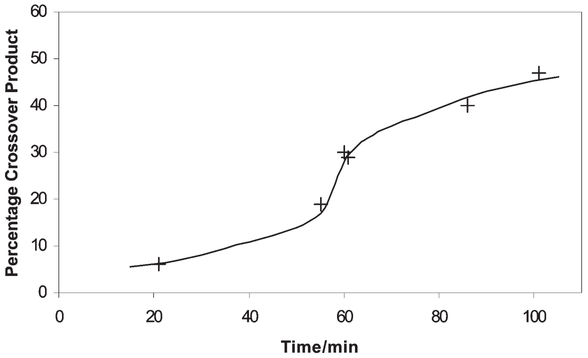


Fig. 6 Plot of amount of cross-over product **11** *versus* pyrolysis time in 'dual FVP' pyrolyses of **6** and **7**.

FVP experiments than has been possible in the past. The main results from the project are as follows:

(i) Temperature–conversion plots are related to activation energy and therefore can provide information on the mechanism of a reaction not available by other methods.

(ii) Increase in background pressure is confirmed to cause an increase in conversion to products.

(iii) Conversion to products is relatively unaffected by throughput rate.

(iv) Packing the furnace tube with inert materials reduces the temperature required for conversion and also increases the slope of the temperature–conversion plot. Different packing materials show different effects but generally show their greatest effect at the exit point of the furnace.

(v) 'Catalysts' can cause reactions to take place under very mild conditions.

(vi) Dimerisation of benzyl radicals takes place predominantly in the gas-phase under our standard FVP conditions, though the site of dimerisation can be altered by variation of throughput rate, furnace temperature or background pressure.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 250 (or 200) and 63 (or 50) MHz respectively for solutions in [^{2}H]chloroform.

Starting materials

The pyrolysis precursors dimethyl 2-[(pyrrol-2-yl)methylidene]-malonate **1**,[4] 1-phenyl-5-*p*-tolyl-1,2,5-triazapentadiene **3**,[8] cinnamaldehyde phenylhydrazone **4**,[9] 1,5-diphenyl-1,5-diazapentadiene **5**,[10] dibenzyl oxalate **7**[18] and di-*p*-tolyl oxalate **10**[18] were made by literature methods.

Flash vacuum pyrolysis experiments

Our standard FVP apparatus is shown in Fig 1 and consists of a borosilicate glass inlet tube (B24 cone lubricated by silicone grease), a horizontal silica furnace tube (35 × 2.5 cm od; B24 sockets) and a borosilicate glass U-tube trap (B24 cone lubricated by silicone grease) situated at the exit point of the furnace. The other end of the U-tube is connected to a short vacuum line consisting of a Pirani gauge, an inlet for dry nitrogen, a second trap, and the vacuum pump.

For the FVP experiment, the precursors were placed in the inlet and were volatilised by heating with a Büchi drying pistol oven. The silica furnace tube was heated by a Carbolite electrical tube furnace and the vacuum was generated by an Edwards rotary pump (pumping speed 100 dm^3 min^{-1}, working pressure *ca.* 10^{-2} mbar). The temperature was measured by a thermocouple situated at the centre of the furnace; typical temperature gradients are quoted in the manufacturer's literature. Products were collected at the exit point of the furnace in the U-tube which was cooled by liquid nitrogen. When the pyrolysis was complete, the pump was isolated and the trap was allowed to warm to room temperature under an atmosphere of dry nitrogen. The trap was detached from the line, [^{2}H]chloroform was distilled into the trap to dissolve the entire pyrolysate and an NMR spectrum was recorded.

Results shown in Table 1, entries 2, 6 and 10, and Table 3, entries 3 and 4, demonstrate a high degree of reproducibility and for this reason FVP experiments were not normally carried out in duplicate. In principle the main source of uncertainty is the measurement of the NMR integral values, normally assumed to be of the order of ±5%, though the results would suggest that the error is probably substantially smaller than this. Variables reported in the Tables include the quantity of substrate, furnace temperature (T_f), inlet temperature (T_i), background pressure (P) and the time required for the complete distillation of the precursor through the furnace (t).

FVP reactions of dimethyl 2-[(pyrrol-2-yl)methylidene]-malonate 1

The precursor **1** was subjected to FVP reactions under the conditions detailed in Table 1. The course of the reaction **1→2** was monitored by ^{1}H NMR spectroscopy in the range δ_H 7.7–7.9; the product **2** is characterised by a doublet at δ_H 7.85 (1H) and the precursor **1** by a singlet at δ_H 7.71 (1H). No other significant products were detected.

FVP reactions of the di- and tri-azapentadienes 3–5

FVP reactions of the precursors **3**–**5** were carried out under the conditions listed in Table 2. The entire pyrolysates were monitored by NMR spectroscopy. These reactions produce relatively complex pyrolysates and so, as a first approximation, the published yields of the cyclised products (at total conversion of precursor) were used to calibrate the conversion at lower temperatures. For **3**, the integral values of the methyl protons of the starting material (δ_H 2.30) and quinoxaline product (δ_H 2.54) were compared. Similarly, signals due to the central H(3) of **5** (δ_H 5.05) and H(2) of quinoline (δ_H 8.55) were distinct in the spectra and were used to assess the conversion. Although this method was not possible in the case of **4**, distinct resonances for precursor and product were identified in the ^{13}C NMR spectra of the pyrolysates; an algorithm was therefore set up using an authentic 1 : 1 mixture of **4** and quinoline which was used to calculate relative intensities and hence the percentage composition of the pyrolysates.

FVP reactions of dibenzyl oxalate 7 and di-*p*-tolyl oxalate 10—'dual' FVP

FVP reactions of the precursors **7** and **10** were carried out under a variety of conditions (see below and Table 3). The entire pyrolysate was dissolved in $CDCl_3$ and analysed by ^{1}H NMR spectroscopy in the range δ_H 2.8–3.0. The methylene protons of bibenzyl **9**, 4-methylbibenzyl **12** and 4,4′-dimethylbibenzyl **13** are well resolved at δ_H 2.93, 2.90 and 2.87 respectively. In some cases *p*-xylylene polymer was formed but this material is insoluble in $CDCl_3$ and therefore does not affect the analysis. For this reason, the cross-over ratio is measured from the amount of 4-methylbibenzyl **12** and 4,4′-dimethylbibenzyl **13**, since the level of the latter provides a measure of the maximum amount of *p*-tolyl radicals available for coupling.

Crossover experiments were performed as follows. First, oxalates **7** and **10** were weighed onto separate aluminium foil trays and laid side by side in the same inlet tube. By raising the inlet temperature to the value appropriate for the *p*-tolyl derivative **10** both compounds volatilised at approximately the same rate.

The apparatus shown in Fig. 5 was used for the 'dual-FVP' experiments. Samples of **7** and **10** were placed in individual inlet tubes and their volatilisation rates were carefully controlled by variation of the temperature of the inlet ovens. Both tube furnaces were set to the same temperature. The pyrolysates from both furnaces were collected in the same trap which was evacuated by an appropriate vacuum system. The 'time' quoted for the pyrolysis (Table 3) was measured from the first appearance of pyrolysate in the trap, until the sublimation of precursor was completed. As before, the pyrolysates were dissolved in $CDCl_3$ and analysed by ^1H NMR spectroscopy in the range δ_H 2.8–3.0.

The high-vacuum result shown in Table 3 (entry 8) was obtained by using an oil diffusion pump in series with the rotary pump and the pressure was measured by a Penning gauge situated on the vacuum line side of the pump. The line, furnace tube and inlet system were degassed for 2–3 h before the FVP experiment.

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References

1 R. F. C. Brown, *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York, 1980.
2 Y. Vallée, *Gas Phase Reactions in Organic Synthesis*, Gordon and Breach, Amsterdam 1997.
3 For example, H. McNab, *Contemp. Org. Synth.*, 1996, 373–396.
4 S. E. Campbell, M. C. Comer, P. A. Derbyshire, X. L. M. Despinoy, H. McNab, R. Morrison, C. C. Sommerville and C. Thornley, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2195–2202.
5 C. L. Hickson and H. McNab, *J. Chem. Res. (S)*, 1989, 176–177.
6 H. McNab and C. Thornley, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2203–2209.
7 H. Hopf and J. Wolff, *Eur. J. Org. Chem.*, 2001, 4009–4030.
8 H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2200–2204.
9 C. L. Hickson and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1569–1572.
10 H. McNab and M. E.-A. Murray, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1565–1568.
11 For a discussion of chemical activation see C. Wentrup, *Reactive Molecules*, Wiley, New York, 1984, p. 225.
12 Ref 1, p. 29.
13 E. L. Moyano and G. I. Yranzo, *J. Org. Chem.*, 2001, **66**, 2943–2947 and references therein.
14 I. Hodgetts, S. J. Noyce and R. C. Storr, *Tetrahedron Lett.*, 1984, **25**, 5435–5438.
15 J. I. G. Cadogan, C. L. Hickson and H. McNab, *Tetrahedron*, 1986, **42**, 2135–2165.
16 E. Hedaya and D. McNeil, *J. Am. Chem. Soc.*, 1967, **89**, 4213–4214.
17 C. L. Angell, E. Hedaya and D. McLeod, Jr., *J. Am. Chem. Soc.*, 1967, **89**, 4214–4216.
18 W. S. Trahanovsky, C. C. Ong and J. A. Lawson, *J. Am. Chem. Soc.*, 1968, **90**, 2839–2842.
19 *cf.* J. I. G. Cadogan, J. B. Husband and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1489–1495.
20 For example, L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, 1957, **79**, 4952–4955.