501. *Studies in Pyrolysis. Part XXI.*[1] *Reaction Mechanisms in the Vapour-phase Pyrolysis of Vinyl Benzoate.*

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The complex pyrolysis of vinyl benzoate is a predominantly homogeneous reaction in the vapour phase (*ca.* 520°), but the decarboxylation route occurs, in part, heterogeneously at a glass surface. No evidence has been found for the existence of free-radical chain-reactions: it seems that the primary reactions occur by mechanisms of some other type. Iodine mildly catalyses the overall rate of decomposition of vinyl benzoate, and strongly catalyses the secondary decomposition of acetophenone (the major degradation product of the ester).

IT has been previously shown qualitatively [1-3] that vinyl benzoate breaks down in the vapour phase (*ca.* 400—550°) by four competing routes. Little quantitative work has been done, other than to place the four reactions in their relative order of importance: R/C^1 (major), C^2 (moderate), A^2 (minor), and B^2 (trace [1]). Only a few tentative conclusions have been advanced [3] about the reaction mechanisms.

In the present work, the problem is approached by a semi-quantitative study of the overall breakdown; the rate of vapour-phase decomposition is measured by following the gas-evolution for various different initial conditions in a static system and comparing it with a standard pressure-time plot.

EXPERIMENTAL

Apparatus and Procedure.—The apparatus (Fig. 1) was essentially a Pyrex glass U-tube reactor, connected to an all-glass high-vacuum line with liquid- and gas-storage vessels. It was supported in a vertical electric furnace F, the bottom of the reactor being located at the pre-determined hot-spot of the furnace. Unless otherwise stated, the hot-spot temperature was 520° ± 3°, measured at the outer wall of the reactor by a chromel-alumel thermocouple.

The pyrolysand (2 ml.) was placed in receiver R and the system evacuated for 30 min. The reactor was then isolated by tap T, the pyrolysand run into the reactor, and the pressure changes followed by a mercury-in-glass manometer. During the run, liquid pyrolysand refluxed steadily in the air-condenser C. When required, foreign gases were introduced before

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[1] Part XX, Muir and Ritchie, preceding paper.
[2] Allan, Forman, and Ritchie, *J.*, 1955, 2717; Allan, Jones, and Ritchie, *J.*, 1957, 524.
[3] Part XVIII, Reininger and Ritchie, *J.*, 1963, 2678.

a run; foreign liquids and solids were added by solution in the pyrolysand. The total effective volume of the system was *ca.* 450 ml., the volume of the reactor to the bridge B being 65 ml.

Gas Analysis.—Gaseous pyrolysates were analysed by transferring a small sample, through a receiver and Toepler pump, to a Sleigh gas-absorption unit.

Preparation of Vinyl Benzoate.—The ester was prepared by ester interchange [4] between vinyl acetate and benzoic acid: careful fractionation yielded a product, b. p. 108°/30 mm., shown by gas-liquid chromatography to contain a little ethylidene diacetate (5—10% in various preparations) which could not be removed without an undesirably long period of refluxing. Since this work was done, it has been found possible to prepare rigorously pure vinyl benzoate; [1] but at the time it was decided to use the slightly crude product, purifying it *in situ* during pyrolysis by allowing the rapid thermal disproportionation [5] of ethylidene diacetate (to acetaldehyde and acetic anhydride) to proceed, removing most of the acetaldehyde by again reducing the pressure to a very low value, and leaving a small quantity of the inert acetic anhydride in the system. (Later, a repetition of some of the work with very pure ester prepared by Dr. W. M. Muir [1] gave closely similar results and confirmed the validity of the above procedure.)

RESULTS

Pressure-Time Curves.—In a typical family of pressure–time curves (Fig. 2), the initial sharp rise in the early minutes corresponds to decomposition of the impurity (ethylidene diacetate); a standard procedure was adopted whereby the pressure was reduced to *ca.* 10 mm. some 3 min. after the run began, subsequent decomposition of ester being followed. The next noteworthy feature of the curves is the apparent autocatalysis, the rate of gas-evolution increasing with time; but this was, in fact, found to be characteristic not of the reaction but of the apparatus, being due to a varying rate of diffusion of vaporised ester from the hot zone of the reactor. In general, a steady maximum rate (expressed in mm./min.) was approached after 50—60 min., and this was considered to be the rate of degradation characteristic of a run.

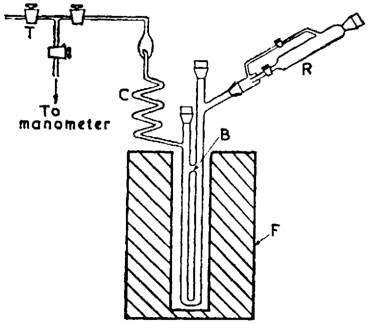

FIG. 1. Diagram of reaction vessel.

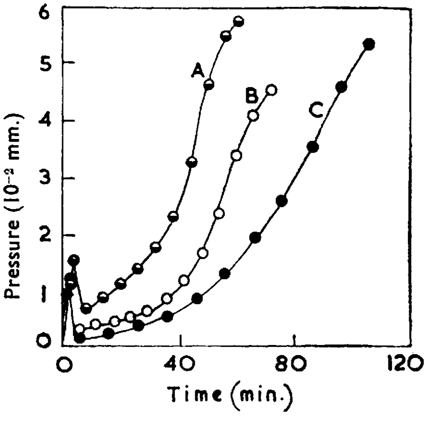

FIG. 2. Typical pressure–time curves for decomposition of vinyl benzoate; A and C. 520°; B, 500°.

With successive pyrolyses, heavy carbonaceous deposits accumulated in the reactor, together with high-boiling breakdown products, including much benzoic acid, and the reaction rate fell sharply (this is due [6] to partial polymerisation of the ester, followed by A^1 scission of the polymer to benzoic acid and a conjugated polyene). Table 1 records results of typical runs. Copyrolysis with 5—10% of benzoic acid markedly depressed the rate. In general, therefore, runs were made in a decarbonised reactor. Although rates tended to be high in new glass, seasoning occurred and the rates were reasonably reproducible after about 15 runs. For rate maxima of 10—20 mm./min., a tolerance of ±2 mm./min. was considered satisfactory. The decarbonising

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[4] Burnett and Wright, *Trans. Faraday Soc.*, 1953, **48**, 1108.

[5] Geuther, *Annalen*, 1858, **106**, 249; Matheson, B.P. 368,835/1930; U.S.P. 1,872,479/1932.

[6] Rashbrook and Taylor, *Chem. and Ind.*, 1962, 265.

procedure finally adopted was to draw a steady stream of air, by means of a water-pump, through the reaction vessel heated at *ca.* 540°, soluble pyrolysis products having previously been washed out in solvents.

Effect of Packing.—Runs in a reactor packed with glass wool gave widely varying rates, ranging from 1·5 to 40 mm./min., as against a blank run of 12 mm./min.; the rates depended on the distribution of the packing. A series of runs was therefore made with the packing restricted to the bottom 20 cm. of the reactor (*i.e.*, that part in which decomposition was taking place, as judged by the zone of carbonisation). Under these conditions, liquid ester refluxed normally in the air-condenser of the reactor: and the rate maxima varied over the much narrower range 15—17 mm./min. The free volume of the reactor was not significantly altered in these runs.

The pyrolysate gas from a run in a packed reactor (Table 3, run 7) shows a carbon dioxide content much higher than normal. The figures for standard conditions are average values, based on a large number of runs in an empty decarbonised reactor.

Pyrolyses over copper turnings, in a reactor coated internally with silica, did not give any rate-deviations from the corresponding blank runs.

Effect of Free-radical Inhibitors and Initiators.—In a carbonised reactor in which the rate had fallen to a very low figure (<1 mm./min.), runs were made in the presence of the following free-radical inhibitors and initiators (0·1% of each): quinol, benzoquinone, toluquinone, azodicyclohexanecarbonitrile, benzoyl peroxide. No changes in the reaction rate resulted, within experimental error. Pyrolysis in a clean reactor, in presence of toluene (1%), gave a similar result.

Pyrolyses in a decarbonised reactor in the presence of nitric oxide (3, 7, 13, and 85 mm.) all gave rates of 11 mm./min., identical with that of the blank run. In the presence of propene (60, 200 mm.) the rates were 11 and 12 mm./min., against blanks of 12 and 14 mm./min., respectively. In these runs, where large pressures of foreign gases were used, blanks were run

TABLE 1.

Effect of carbonaceous deposits on the reactor wall on the rate of pyrolysis of vinyl benzoate (series of 15 consecutive runs at 520°).

Run no.	1	2	5	15
Max. rate (mm./min.)	17	8	1·5	0·75

TABLE 2.

Effect of added iodine (1%) on the rate of pyrolysis of vinyl benzoate at 520°.

Run	Conditions	Max. rate (mm./min.) With iodine	Control
1	Carbonised reactor	2	0·75
2	Decarbonised reactor	20	10
3	Decarbonised reactor *	15	5

* Pressure rose to 270 mm. and was then reduced to remove acetaldehyde before proceeding with run.

TABLE 3.

Composition of gaseous pyrolysates (vol. %).

Run	Conditions	CO	CO_2	Acetylene	Olefin *	CO/CO_2 (molar)
1	Standard (av. values)	76·5	14·5	6·0	3·0	5·2
2	Standard (reaction stopped at 60 mm. abs. pressure)	76·6	15·2	4·5	3·7	5·0
3	Standard (reaction stopped at 200 mm. abs. pressure)	76·8	15·9	4·3	3·0	4·8
4	With nitric oxide (14 mm.)	76·5	11·8	8·5	3·2	6·5
5	With nitric oxide (31 mm.)	76·3	12·1	7·5	4·1	6·3
6	With propylene (60 mm.)	66·2	15·2	4·9	18·7 ‡	4·4
7	Packed reactor	64·5	31·4	1·8	2·3	2·1
8	With iodine (1%)	79·7	15·1	2·1	3·1	5·3

* The olefin, characterised [2] as ethylene, appears consistently in all pyrolysates as a minor component. Its origin is not known. ‡ Olefinic fraction mainly added propene.

after addition of equivalent pressures of nitrogen, to compensate for the inert-gas effect which caused the maximum rate to be attained more rapidly than in a normal run.

Effect of Iodine.—Addition of iodine (1%) to vinyl benzoate had a distinct effect on the rate of gas-evolution (Table 2). In run 3 the initial pressure was allowed to reach 270 mm. before being reduced again to a low figure, to ensure complete destruction of any residual ethylidene diacetate in the system and subsequent removal of acetaldehyde. The decomposition of aldehydes is known to be affected by the presence of iodine.[7]

The effect of iodine on the decomposition rate of acetophenone (the major reaction-product) was very marked. Pyrolysis of the ketone (2 ml.) gave a pressure rise of only 2 mm. after 40 min.; but pyrolysis in presence of iodine (1%) gave an immediately measurable decomposition, a rate maximum of 23 mm./min. being reached in 50 min.

In these catalysed runs, noticeably heavy carbonaceous deposits were obtained. A similar qualitative effect has been reported for the catalysed pyrolysis of acetone.[8]

Gas Analysis.—Analyses of the pyrolysate gases are given in Table 3.

DISCUSSION

The results reveal the general nature of the pyrolysis of vinyl benzoate, although the limitations of the technique precluded a fuller study of the reaction.

Two decomposition routes are homogeneous vapour-phase reactions—the major R/C^1 reaction, and the minor A^2 reaction, measured respectively by the carbon monoxide and acetylene evolved. The rather high rate-values obtained in a partly packed reactor are ascribed to a partly heterogeneous decarboxylation (C^2 scission) of the ester, here shown by the high carbon dioxide content of the gaseous pyrolysate. However, this reaction itself must be mainly homogeneous, since a very large increase in the surface : volume ratio in the reactor increased the carbon dioxide figure by a factor of only about 2.

There is no evidence that radical chains play a significant part in the overall decomposition; established free-radical agents neither promote nor inhibit the reactions: also, no surface-termination effects were observed. Moreover, the breakdown does not yield the complexity of products predictable by plausible chain-mechanisms; and all the available evidence strongly suggests that the separate routes all occur by molecular mechanisms (cf. the four-centre[2] and six-centre[3] transition states suggested respectively for the R/C^1 and A^2 scissions). Finally, there is also some evidence[3] that C^2 scission of vinyl esters is predominantly intramolecular in mechanism, although the possibility cannot be excluded that there is competition by a very minor mechanism of another type.

The gas analyses in Table 3 indicate that the three main reactions occur to approximately the following extents: R/C^1, 76%; C^2, 15%; A^2, 6%. The balance of some 3% is accounted for by the unknown minor reaction producing ethylene,[2] and by the trace of B^2 scission[1] (which is so small that it has been neglected in the present work). These figures agree reasonably with those given by Reininger and Ritchie,[3] if the latter results are corrected for polymer formation and the presence of secondary products.

The catalysis of ester decomposition by iodine has previously been reported[9] for methyl formate and acetate. In the present work, the effect is relatively small, the rate maximum being increased by a factor of between 2 and 3. The accelerated rate was immediate, and therefore could not have been due solely to the secondary decomposition of acetophenone. The mechanism of the catalysed reaction cannot be defined in precise terms. Other evidence does not suggest that free-radical reactions are being induced. In addition, the catalysis affects the *complete* reaction scheme, since the gas analyses (cf. Table 3, run 8) do not indicate that the rate of any one route is being significantly accelerated with respect to the other routes. Activation of the ester itself must therefore be occurring. Bairstow and Hinshelwood[7] have previously suggested that activation by collision is favoured by

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[7] Bairstow and Hinshelwood, *Proc. Roy. Soc.*, 1933, *A*, **142**, 77.

[8] Gantz and Walters, *J. Amer. Chem. Soc.*, 1941, **63**, 3412.

[9] Bairstow and Hinshelwood, *J.*, 1933, 1147.

the dipole moment of the ester acting in conjunction with the polarisable structure of iodine, and such an explanation seems most likely in the present case.

The very marked catalysis of the acetophenone decomposition is of interest: for, although the catalytic effect of iodine in the decomposition of aldehyde has been reported as general, acetone,[8,10] ethyl methyl ketone,[8] and diethyl ketone are the only ketones previously observed to undergo this effect.

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[10] McNesby, Davis, and Gordon, *J. Amer. Chem. Soc.*, 1954, **76**, 823.