

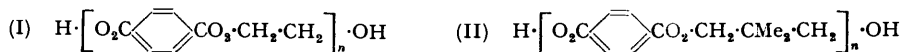
Studies in Pyrolysis. Part IV. Model Systems for the Pyrolysis of Poly(ethylene Terephthalate) and Allied Polyesters.*

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Ethylene dibenzoate breaks down in the vapour phase (*ca.* 400—550°) by two competitive routes: (i) a major acyl-oxygen scission (A^1) to benzoic acid and vinyl benzoate, and (ii) a minor disproportionation (D) to benzoic anhydride and acetaldehyde. The vinyl benzoate formed then pyrolyses by three competitive routes: (i) a major thermal rearrangement (R) to benzoyl-acetaldehyde, which then undergoes decarbonylation (C^1) to carbon monoxide and acetophenone; (ii) a minor alkenyl-oxygen scission (A^2) to benzoic acid and acetylene; and (iii) a minor decarboxylation (C^2) to carbon dioxide and styrene. Separate pyrolysis of benzoyl-acetaldehyde confirms the R/C^1 stage. Acyl-oxygen scission of vinyl benzoate to benzaldehyde and keten does not occur; but aliphatic vinyl esters (*e.g.*, acetate and isobutyrate) are pyrolysed not only *via* routes A^2 , C^2 , and R/C^1 , but also by a fourth competitive route—a major acyl-oxygen scission (B^1) to acetaldehyde and a keten corresponding to the acyl group. The bearing of these results on the pyrolysis of cognate polyesters is discussed.

THE thermal stability of various synthetic polyesters, such as poly(ethylene maleate) and the polyester fibres (*e.g.*, "Terylene" and "Dacron") based on poly(ethylene terephthalate) (I), is of great technological importance. Various studies on the thermal degradation of the latter polymer have been published, but the precise mechanism of breakdown remains obscure. Pohl (*J. Amer. Chem. Soc.*, 1951, **73**, 5660) followed the change by measuring the rate of gas-evolution, and showed that at *ca.* 300° in the absence of oxygen the polyester undergoes random main-chain scission, with progressive reduction in molecular weight. The pyrolysate contained acetaldehyde, water, and carbon dioxide, as well as carboxyl and anhydride groups. He deduced that a principal point of weakness in the chain is the β -methylene group, since the polyester (I) is markedly less thermostable than its analogue (II), which possesses no β -hydrogen atoms.



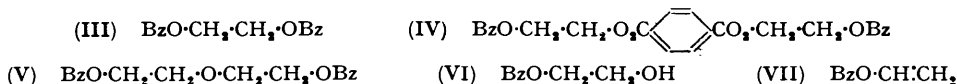
Marshall and Todd (*Trans. Faraday Soc.*, 1953, **49**, 67) studied the kinetics of the degradation (*ca.* 280—320°) by following changes in the viscosity of the molten material. Like Pohl, they deduced a random chain scission, probably at the ester linkages, giving rise to one carboxyl group per scission, and detected acetaldehyde and carbon dioxide in the pyrolysate. In addition, they detected carbon monoxide, terephthalic acid, and another solid product (not positively identified). They concluded that degradation is essentially free-radical in character, and outlined a tentative sequence of propagation reactions.

These quantitative studies cannot yet be fully interpreted, however, in the absence of a full *qualitative* identification of the degradation products. The present work was planned to provide this identification.

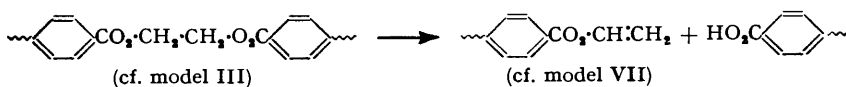
Difficulties encountered in preliminary experiments with the polyester (I) itself suggested as a promising alternative approach the pyrolysis of simplified model systems representing (i) specific segments (*e.g.*, III, IV, V) from within the intact polyester chain (I); (ii) terminal segments of (I) bearing hydroxyl (*e.g.*, VI) and carboxyl end-groups; and (iii) terminal segments of the pyrolysed chain bearing new end-groups which might be predicted *a priori* (*e.g.*, VII). The reasons for selecting (III), (IV), and (VI) are evident from formula (I), while (V) represents the known incorporation of occasional ether linkages (*e.g.*, diethylene glycol

* Part III, *J.*, 1935, 1054.

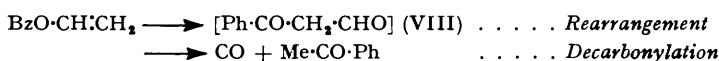
units) into the original chain during polycondensation. Vinyl benzoate (VII) was selected because the model compound (III) had been reported to yield vinyl benzoate and benzoic acid when pyrolysed at 360—425° (Chitwood, U.S.P. 2,251,983/1941), in conformity with



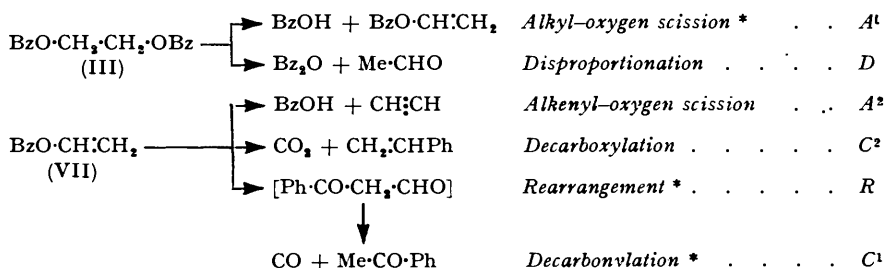
the normal pyrolytic scission to olefin and carboxylic acid undergone by simple alkyl carboxylates (cf. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chap. 17). This clearly suggests that each random chain-scission should generate concurrently a carboxyl end-group (cf. Marshall and Todd, *loc. cit.*) and a vinyl ester end-group, for which vinyl benzoate is an obvious model, thus :



Re-investigation of Chitwood's results by Allan and Ritchie (*Chem. and Ind.*, 1953, 747) showed that the vinyl benzoate and benzoic acid produced from ethylene dibenzoate on pyrolysis are accompanied by carbon monoxide and acetophenone, and that these by-products, not recorded by Chitwood, are also formed on pyrolysis of vinyl benzoate alone. The results strongly suggested that vinyl benzoate is pyrolysed by primary thermal rearrangement into its isomeric β -keto-aldehyde, benzoylactaldehyde (VIII), and that this, in turn, yields acetophenone by the normal pyrolytic decarbonylation of aldehydes (cf. Hurd, *op. cit.*, Chap. 10) :



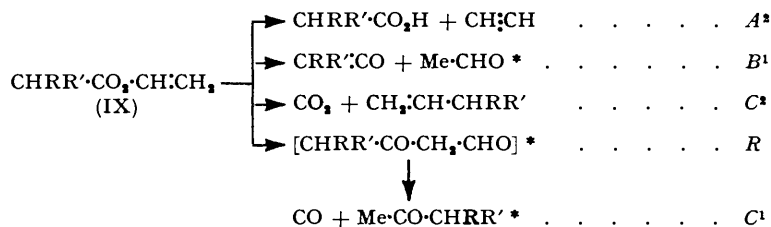
Extension of these studies has now shown that the pyrolysis of ethylene dibenzoate and vinyl benzoate at *ca.* 400—550°, in a Pyrex-glass flow-reaction vessel, is even more complicated than at first thought. The constituents now identified in the complex pyrolysates from (III) and (VII), and their relative abundance, are best accounted for by the following series of competitive and consecutive reactions, where * indicates the predominant routes :



With the exception of benzoylactaldehyde, all the products shown above were identified in the pyrolysate from (III); in addition, benzene, methane, and small amounts of ethylene were detected. Benzene and methane are readily accounted for as secondary breakdown products of benzoic acid (from A^1 and A^2) and acetaldehyde (from D) respectively; but no obvious route suggests itself for the formation of ethylene, and this product [from (III) and (VII), but not (VIII)] still remains unexplained.

Just as vinyl benzoate is a suitable model compound for studying the pyrolysis of the aromatic polyester (I), so also can aliphatic vinyl carboxylates such as vinyl acetate (IX; R = R' = H) and isobutyrate (IX; R = R' = Me) be used to study the end-groups which are formally possible if a purely aliphatic polyester [*e.g.*, poly(ethylene maleate)] also undergoes primary alkyl-oxygen scission. It has now been found that at *ca.* 500—550°

the ester (IX) breaks down by the following system of four concurrent competing primary scissions, where * again indicates the predominant routes :

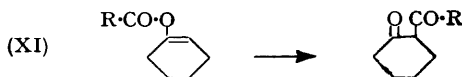
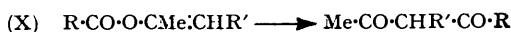


Three of these primary routes (A^2 , C^2 , and R/C^1) are parallel to those found for vinyl benzoate : but a major acyl-oxygen scission (B^1) now appears, which has no counterpart with the aromatic ester. With the exception of the β -keto-aldehyde, all the products shown were identified in the pyrolysate from (IX) ; in addition, there were small quantities of methane and ethylene, which are subject to the comments made above on the pyrolysate from the ester (III).

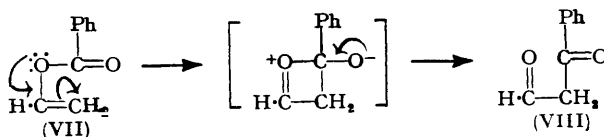
No systematic search was made for specific catalytic effects at the wall of the reaction vessel ; but comparative runs were made with vinyl acetate in three vessels constructed respectively of Pyrex glass, Vitreosil, and stainless steel. For the first two, the results were qualitatively the same, though Vitreosil somewhat enhanced route R/C^1 at the expense of B^1 (see Table 4) ; but the gaseous pyrolysate from the stainless-steel vessel contained some 46% of hydrogen. A similar experiment with vinyl benzoate in a stainless-steel vessel also yielded hydrogen (*ca.* 12%). Several sources of this hydrogen are possible ; but it probably arises from (VII) mainly by a catalysed pyrolysis of the ethylene which has been shown to occur in the pyrolysate from vinyl carboxylates. Pure ethylene, pyrolysed under the same conditions in the same vessel, yielded hydrogen and paraffin (calculated as methane) in almost the same molar ratio (1 : 1.9) as that observed in the gaseous pyrolysate from vinyl benzoate itself (1 : 1.8). In the pyrolysis of vinyl acetate, a further important source of hydrogen is probably the acetone formed *via* route R/C^1 : for acetone, pyrolysed alone under the same conditions, yielded a large amount of hydrogen.

DISCUSSION

Route R/C¹.—The mechanism of the unexpected conversion of vinyl carboxylates into carbon monoxide and a methyl ketone, which is the most important result emerging from the present work, is suggested by the fact that many enol carboxylates (*e.g.*, X ; R = Me or Ph, R' = H : XI ; R = Me) undergo intramolecular rearrangement at *ca.* 500° to an isomeric β -diketone (Boese and Young, U.S.P. 2,395,800/1946 ; B.P. 615,523/1949 ; Young, Frostick, Sanderson, and Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 3635). *cycloHex-1-enyl benzoate* (XI ; R = Ph) rearranges similarly, yielding chiefly 2-benzoylcyclohexanone at *ca.* 480° (Allan and Ritchie, unpublished observation, 1953) ; and an analogous thermal rearrangement at 240° of the enol carboxylate (X ; R = Me, R' = CO₂Et) provides a further example in this category (Wislicenus, *Ber.*, 1905, **38**, 546).

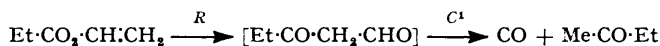


Young *et al.* (*loc. cit.*) proposed a plausible intramolecular mechanism for the thermal rearrangement of enol carboxylates, *via* a cyclic transition state, which can be applied to vinyl benzoate as follows :



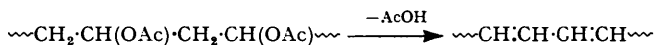
No *direct* evidence for this rearrangement was obtained by Allan and Ritchie (*loc. cit.*), which is not surprising in view of the known instability of (VIII) (Claisen and Fischer, *Ber.*, 1887, **20**, 2191; von Bülow and Sicherer, *Ber.*, 1901, **34**, 3889). Nevertheless, *indirect* confirmation is provided by the fact that (VIII) breaks down at 400–550° into carbon monoxide and acetophenone. The gaseous pyrolysate consists of carbon monoxide (*ca.* 95–97%), with a small amount (*ca.* 2–5%) of carbon dioxide; but in view of the great difficulty of purifying the keto-aldehyde (VIII) rigorously it is uncertain whether the carbon dioxide is due to a true minor side-reaction, or to impurity. Even this indirect confirmation cannot be provided in the case of aliphatic vinyl carboxylates such as vinyl acetate (IX; R = R' = H), since the corresponding β -keto-aldehyde (acetoacetaldehyde) is here incapable of free existence, condensing spontaneously to 1 : 3 : 5-triacetylbenzene (Claisen and Stylos, *Ber.*, 1888, **21**, 1144). Nevertheless, the most convincing explanation of the observed acetone (from vinyl acetate) and methyl *isopropyl* ketone (from the *isobutyrate*) is once again route R/C^1 .

The previously unexplained by-products reported by Chitwood (*loc. cit.*) in the pyrolysis of ethylene diacetate and dipropionate can now be readily accounted for on the basis of competing A^2 , B^1 , C^2 , and R/C^1 scissions of vinyl carboxylates. For example, the formation of ethyl methyl ketone from ethylene dipropionate can be attributed to secondary R/C^1 breakdown of vinyl propionate, thus :

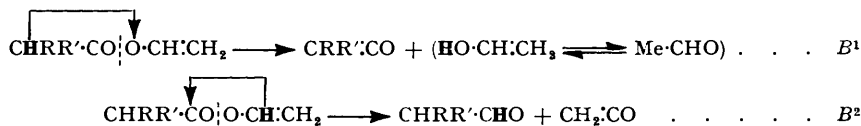


When the acetophenone content of the pyrolysate from vinyl benzoate is plotted against reaction temperature (range 300–550°) the relationship is almost linear (see Table 2); and extrapolation to zero acetophenone content suggests *ca.* 190° as the threshold temperature for decomposition—*i.e.*, slightly below the b. p. of vinyl benzoate (203°/760 mm.). Since the usual preparations of this ester entail either a vapour-phase reaction, or some other high-temperature process, and since vinyl benzoate and acetophenone have almost the same b. p., the preparation of really pure ester is likely to be difficult. It has, in fact, now been found that vinyl benzoate prepared at *ca.* 300–350° by the catalysed vapour-phase addition of acetylene to benzoic acid (B.P. 581,501/1946) contains up to *ca.* 7% of acetophenone.

Routes A¹ and A².—Alkenyl-oxygen scission (A^2) of an alkenyl carboxylate to an acetylene and a carboxylic acid does not seem to have been observed previously, although alkyl-oxygen scission (A^1) is a well-established major route (though not the only one) in the pyrolysis of alkyl carboxylates. It is of interest that, although monomeric vinyl acetate breaks down thermally by four competitive routes (A^2 , B^1 , C^2 , and R/C^1), yet its polymer has been shown by Grassie (*Trans. Faraday Soc.*, 1952, **48**, 379; 1953, **49**, 835) to break down *in vacuo* at *ca.* 215–235° almost wholly by evolution of acetic acid, *via* a non-radical chain reaction. Each successive step is the normal A^1 scission of an alkyl carboxylate, the olefinic product here being a polyacetylene, thus :



Route B¹.—It is clear that there are two formally possible modes of acyl-oxygen scission of an aliphatic vinyl carboxylate (IX), each yielding a keten and an aldehyde, thus :



For vinyl acetate (R = R' = H) it happens that both routes lead to the same pair of products, keten and acetaldehyde (both found in the pyrolysate), so that here it is not possible to say which route is followed; for aliphatic esters higher than the acetate,

however, routes B^1 and B^2 are no longer equivalent. It is found that vinyl isobutyrate ($R = R' = \text{Me}$) yields acetaldehyde and secondary products attributable to dimethylketen (route B^1), with no detectable quantity of isobutyraldehyde and keten (route B^2). Route B^1 is structurally precluded for vinyl benzoate, which lacks the necessary α -hydrogen atom in the acyl group; yet, although B^2 is still formally possible, the benzoate shows no type of acyl-oxygen scission, benzaldehyde and keten being entirely absent from the pyrolysate. The inference is that vinyl carboxylates in general can undergo acyl-oxygen scission by route B^1 only.

Only one of the B^1 products from vinyl isobutyrate was identified directly (acetaldehyde); there was no direct evidence for the dimethylketen which should have accompanied it. Presumably the latter failed to survive passage through the reaction vessel at 550° ; and it has, in fact, been shown to break down at high temperatures into propene and 2:3-dimethylbut-2-ene (Staudinger, "Die Ketene," F. Enke, Stuttgart, 1912, p. 142; Staudinger and Endle, *Ber.*, 1913, **46**, 1437).

The gaseous pyrolysate from vinyl isobutyrate contained both propene and 2:3-dimethylbut-2-ene, which very strongly confirms that dimethylketen is a transient primary product in the pyrolysis.

In addition to the various constituents detailed previously, the pyrolysate from vinyl acetate contained a small amount of acetic anhydride, whereas that from vinyl isobutyrate contained no acid anhydride. The acetic anhydride may have arisen either by combination of acid (from A^2) with keten (from B^1), or by direct pyrolysis of the acid (cf. Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515). The former explanation is favoured by the absence of isobutyric anhydride; for although keten itself largely survives passage through the reaction vessel, the much less stable dimethylketen is represented only by its breakdown products, and would therefore not be expected to combine significantly with the free isobutyric acid.

Route C².—From vinyl isobutyrate, route C^2 should have yielded carbon dioxide and 3-methylbut-1-ene. The latter could not be identified positively from the infrared spectrum of the gaseous pyrolysate, owing to masking effects; but two of its isomers were identified, *viz.*, 2-methylbut-1-ene (weak) and 2-methylbut-2-ene (strong), and it is highly probable that these are due to thermal isomerisation of the primary olefin to a mixture of isomeric pentenes.

The direct decarboxylations of esters recorded in this paper are of considerable interest; for, although thermal decarboxylation of acids is well established, only very few esters have been reported to show this behaviour (see, *e.g.*, Skraup and Beng, *Ber.*, 1927, **60**, 942).

Route D.—The formation of small amounts of benzoic anhydride and acetaldehyde from the ester (III) cannot be attributed to secondary breakdown of substances (VII) and (VIII) as intermediates, since neither yields the anhydride or aldehyde when pyrolysed separately under the same conditions. Further, although Davidson and Newman (*loc. cit.*) have demonstrated the pyrolytic production of anhydrides from a wide range of carboxylic acids, including benzoic acid, conversion of this acid into its anhydride is insignificant under the conditions now employed. It therefore seems that benzoic anhydride and acetaldehyde must be produced simultaneously by a minor competitive scission (D) of (III), analogous to certain other thermal disproportionations whereby esters yield an acid anhydride as one scission product (Geuther, *Annalen*, 1858, **106**, 249; Hurd and Bennett, *J. Amer. Chem. Soc.*, 1929, **51**, 1197).

It may be noted that Deutsch and Hermann (G.P. 515,307/1927), who briefly described the breakdown of vinyl acetate at *ca.* 470° over an activated carbon catalyst, recorded that, in addition to constituents which have all now been observed in the uncatalysed thermal decomposition of the ester (acetaldehyde, acetone, keten, acetic acid and anhydride, and unspecified hydrocarbons), the pyrolysate also contained "vinyl-äther." It should therefore be emphasised that no divinyl ether was observed in any of the pyrolyses now studied, so that disproportionation of vinyl carboxylates to acid anhydride and divinyl ether is not one of the purely thermal competitive breakdown routes.

Application of Results to Polyesters.—Since the model compounds studied were all

pyrolysed in the vapour phase, the results must be applied with some caution in interpreting the recorded pyrolyses of poly(ethylene terephthalate), which were effected with molten polymer. Nevertheless, our results suggest a straightforward explanation for many previous observations—for example, (i) the copious evolution of carbon monoxide on pyrolysis of poly(ethylene terephthalate) (a fact not hitherto explained, and not mentioned by Pohl, *loc. cit.*), (ii) the formation of carboxyl and anhydride groups and of acetaldehyde, and (iii) the absence of vinyl ester groupings from the pyrolysate (Pohl, *loc. cit.*; Marshall and Todd, *loc. cit.*; Gilchrist and Ritchie, unpublished observations, 1951). One consequence of this last observation requires emphasis. Chitwood (*loc. cit.*) pyrolysed the ester (III) by refluxing it at 360–425°, using a take-off head at 220–245° to remove vinyl benzoate as formed. In other words, the contact time was comparatively short; and it was shorter still in the vapour-phase flow-reaction vessels now used. Under these conditions, most of the vinyl benzoate formed in the primary scission remained undecomposed; whereas in experiments with molten poly(ethylene terephthalate) (cf. Marshall and Todd, *loc. cit.*), the effective “contact time” is very great, facilitating destruction of any primary vinyl ester groups by secondary pyrolysis of the type now described. On this basis, ketonic products would be expected to accumulate in the molten polyester; and this prediction is now under investigation.

The pyrolysis of the model compounds (IV), (V), and (VI) will be described in later communications.

EXPERIMENTAL

Apparatus.—Five different reaction vessels were used—three of Pyrex glass (P.1, P.2, P.3), one of stainless steel (S), and one of Vitreosil (V). The first four were packed with Pyrex-glass helices, and the fifth with coarsely crushed Vitreosil; P.1, S, and V had approximately the same dimensions (length 65 cm., bore 2 cm.); P.3 had the same bore, but was only 30 cm. long; P.2 was 65 cm. long, with a central section (length 18 cm.) of 2-cm. bore, and inlet and outlet sections of 1-cm. bore.

Each vessel was supported vertically inside a cylindrical electric furnace, which kept the central section of the reaction vessel (about half of its length) at a temperature controlled ($\pm 5^\circ$) by a Variac transformer, and measured by a chromel–alumel thermocouple in a pocket located axially within the reaction vessel. Before each pyrolysis the system was several times evacuated and filled with nitrogen, to avoid combustion of the vapours. The pyrolysate was run into the vessel from a tap-funnel fitted with the usual device for equalising pressures above and below the feed-liquid, and enclosed in a heating jacket to melt solid materials (*e.g.*, III). Liquid (and solid) pyrolysates were collected in a first receiver, *via* an inclined air-condenser; the exit-gases were then passed through a water-condenser to a second receiver cooled in Drikold–acetone; the final uncondensed gases were then passed (through specific reagent-traps as required) to an automatic device which collected them over saturated aqueous magnesium chloride.

Analytical Methods: Results.—Aldehydes and ketones were estimated by Iddles and Jackson's method (*Ind. Eng. Chem. Anal.*, 1934, **6**, 454), and, unless otherwise stated, were identified by their 2:4-dinitrophenylhydrazones and/or semicarbazones (mixed m. p.). All other solid materials were also identified by mixed m. p. Ethylene, propene, and acetylene in unsaturated hydrocarbon fractions were estimated individually in some runs, by Hurd and Spence's method (*J. Amer. Chem. Soc.*, 1929, **51**, 3353). The normal chemical examination of pyrolysate fractions was in many cases supplemented by infrared spectrometry.

Tables 1 and 3 summarise the experimental conditions for 13 runs. They show the amount of liquid pyrolysate (*a*) from each, and the amount and composition of the final gaseous pyrolysate (*b*) collected in the receiver; all gas analyses are reported on a nitrogen-free basis. Details of the examination of (*a*) are given separately below for each pyrolysis.

Ethylene Dibenzoate (III).—Ethylene glycol was benzoylated in acetone solution, and the product precipitated with alkali. Recrystallisation (benzene) gave pure (III), m. p. 72–73° (lit. 73°).

Pyrolysis 1 (vessel P.1). Distillation of (*a*) yielded (i) benzene (2.5 g.; characterised as *m*-dinitrobenzene), (ii) a fraction, b. p. 202–203°/760 mm. (14.5 g.), consisting of (VII) (52% : infrared spectrum; saponified to sodium benzoate and an acetaldehyde resin), acetophenone (38%), and benzoic acid (10%), and (iii) benzoic acid (17 g.).

Pyrolysis 2 (vessel P.2). A trace of acetaldehyde collected in the cold trap. Distillation of (a) removed 12 g. of liquid; the residue, freed from benzoic acid by alkali, was extracted with cold ethanol, and the filtrate evaporated (cold) in a current of air. The final residue became blue, indicating an acid anhydride, on treatment with (*p*-nitrobenzamido)phenylacetic acid (Davidson and Newman, *loc. cit.*), and was identified (infrared spectrum) as benzoic anhydride.

Vinyl Benzoate (VII).—Prepared as described in B.P. 581,501/1946 (b. p. 203°/760 mm., 72—74°/3 mm.), various batches were found to contain between 2% and 7% of acetophenone (Iddles and Jackson's method, *loc. cit.*). This was allowed for in calculating the additional ketone produced on pyrolysis.

TABLE 1. *Pyrolysis of ethylene dibenzoate, vinyl benzoate, and benzoylacetaldhyde.*

Pyrolysis No.	Ethylene dibenzoate		Vinyl benzoate			Benzoyl-acetaldehyde	
	1	2	3	4	5	6	7
Reaction vessel	P.1	P.2	P.1	P.2	P.1 *	P.1	P.2
Temp.	550°	500°	550°	500°	500°	550°	400°
Feed rate (g./min.)	0.40	0.40	0.40	0.27	0.30	0.50	0.33
Weight pyrolysed (g.)	99	50	40	50	40	40	40
(a) Liquid pyrolysate (g.)	72	46.5	28	40	26.5	31.5	34
(b) Gaseous pyrolysate (l.) ...	7.5	2.5	8	6	9	5	4
Composition (%) of (b) :							
Carbon dioxide	†	14.3	20	8.5	13.8	5	2
Carbon monoxide	†	82.1	75	73	64.7	95	97
Hydrogen	—	Nil	Nil	Nil	12.3	Nil	Nil
Methane	—	Nil	Trace?	Trace	6.8	Nil	Nil
Unsat. hydrocarbons (total) ...	—	3.5	ca. 5	18	2.3	Nil	1

* Reaction vessel packed with stainless-steel turnings. † Detected qualitatively. — Not examined.

TABLE 2. *Formation of acetophenone from vinyl benzoate as a function of reaction temperature.*

Reaction vessel	P.2	P.2	P.2	P.2	P.2	P.1
Feed rate (g./min.)	0.25	0.27	0.30	0.30	0.27	0.40
Temp.	300°	350°	400°	500°	500°	550°
Acetophenone (% found)	8.0	10.5	16.5	21.8	19.0	26.0
Acetophenone (% calc.)	7.7	11.3	14.8	21.8	21.8	25.4

Pyrolysis 3 (vessel P.1). Distillation of (a) yielded (i) benzene (1 g.; characterised as *m*-dinitrobenzene), (ii) a liquid, b. p. 64—110°/40 mm. (15 g.), (iii) a liquid, b. p. 110—130°/40 mm. (1 g.), and (iv) benzoic acid (1 g.). Fractions (ii) and (iii) combined contained 26% (corrected) of acetophenone. No benzaldehyde could be detected in (a). The gaseous pyrolysate (b) contained acetylene (infrared spectrum), but no keten (aniline-ether trap) or divinyl ether (infrared spectrum).

Pyrolysis 4 (vessel P.2). Distillation of (a) yielded liquids (i) b. p. 22—66°/4 mm. (2 g.), (ii) b. p. 66—72°/1 mm. (2 g.), (iii) b. p. 72—80°/1 mm. (22 g.), and (iv) b. p. 80°/1 mm. (10 g.). Fractions (i) and (ii) were found (infrared spectrum) to contain (VII), acetophenone, and much styrene; (iii) contained the same constituents, but with less of styrene; (iv) contained benzoic acid. The acetophenone content of (a) was 19% (corrected); there was no benzaldehyde. The gaseous pyrolysate (b) contained ethylene and acetylene (infrared spectrum), but no keten (aniline-ether trap).

Pyrolysis 5 (over stainless steel). For this run only, the vessel P.1. was packed with stainless-steel turnings instead of Pyrex-glass helices. No benzaldehyde could be detected in (a), which was not otherwise examined; keten was absent from the exit gases. A heavy carbonised deposit formed in the reaction vessel.

The acetophenone content of the pyrolysate from six different runs (including four not detailed in Table 1) is shown in Table 2; it is approximately related to reaction temperature *T*, over the range 300—550°, by the linear expression $T = 190 + 14.2$ (acetophenone content). This relationship is only very approximate, in view of the slight variation in experimental conditions.

Benzoylacetaldhyde (VIII). Ethyl formate (1.5 mole) and acetophenone (1 mole) were

treated with sodium ethoxide (0.5 mole) in dry ether (100 g.) as described by von Bülow and Sicherer (*loc. cit.*). The resultant sodium salt was converted into the sparingly soluble copper salt; this was filtered off and washed, and (VIII) was liberated from it by cautious acidification with cold dilute mineral acid. Three separate preparations gave slightly impure (VIII), with concordant analyses [Found: C, 74.3; H, 5.7%; equiv. (alkaline hydrolysis), 175. Calc. for $C_9H_8O_2$: C, 73.0; H, 5.4%; equiv., 148]. It was characterised as its phenylhydrazone (mixture of isomers), m. p. 124—126° (decomp.) (Found: N, 11.9. Calc. for $C_{15}H_{14}ON_2$: N, 11.8%). Von Auwers and Schmidt (*Ber.*, 1925, 58, 536) quote m. p. 126° (decomp.). Owing to its instability, crude (VIII) could not be further purified by fractionation *in vacuo*; 20—30% of a small batch could be distilled at 94—98°/1 mm. (Found: C, 74.3; H, 5.8%), but thereafter water was liberated during distillation, and at least 33% of the batch became wholly resinified. A small quantity of 1:3:5-tribenzoylbenzene, m. p. 116—117° (from ethanol), which is a known condensation product of (VIII), separated from the crude (undistilled) keto-aldehyde (Found: C, 83.4; H, 4.8. Calc. for $C_{27}H_{18}O_3$: C, 83.1; H, 4.7%). Claisen (*Annalen*, 1894, 281, 306) quotes m. p. 118°. Calculations based on the equivalent weight and analytical figures suggest, therefore, that the crude (VIII) is contaminated with 11—13% of this triketone.

Pyrolysis 6 (vessel P.1). Distillation of (a) yielded (i) acetophenone, b. p. 110—116°/55 mm. (27 g.; infrared spectrum), and (ii) a tarry residue (3—4 g.).

Pyrolysis 7 (vessel P.2). Distillation of (a) yielded (i) acetophenone, b. p. 58—70°/3 mm. (15.5 g.), (ii) a liquid, b. p. 90—100°/3 mm. (6.5 g.) consisting of (VIII) together with a little acetophenone (infrared spectrum), and (iii) a brown resin (12 g.).

TABLE 3. *Pyrolysis of vinyl acetate and isobutyrate.*

Pyrolysis No.	Vinyl acetate					Vinyl iso-
	8	9	10	11	12	butyrate
Reaction vessel	P.1	P.1	S	S	V	P.3
Temp.	550°	550°	500°	500°	550°	550°
Feed rate (g./min.)	0.15	0.16	0.57	0.76	0.34	0.08
Weight pyrolysed (g.)	32	85.8	102	91.1	86	9.2
(a) Liquid pyrolysate (g.)	49.5	60.6	13.9	13.8	54	5.6
(b) Gaseous pyrolysate (l.)	10.2	13.4	94.5	58	25.6	2.1
Composition (%) of (b) :						
Carbon dioxide	4.1	3.3	2.6	7.5	3.2	2.4
Carbon monoxide	84.2	88	39.4	36	81.7	67.5
Hydrogen	Nil	Nil	46.1	45	Nil	Nil
Methane	5.1	5	11.5	10	8.2	18.9
(c) Unsat. hydrocarbons (total)	4.6	3.7	0.4	0.8	6.9	11.2
Approx. molar ratio of unsat. hydrocarbons in (c) :						
Ethylene	0.6	—	—	—	0.4	0.8
Propene	0.1	—	—	—	0.1	0.1
Acetylene	0.3	—	—	—	0.5	0.1

Vinyl acetate (IX; R = R' = H). Redistilled commercial ester (*ex* Shawinigan Ltd.) was used.

Pyrolysis at 420° and 700° (vessel P.1). Preliminary runs established the optimum temperature at *ca.* 550°, and showed that virtually no decomposition occurs at 420°, while at 700° strong secondary decompositions occur. For example, at 700°, propene disappears from the pyrolysate, and the methane content of (b) rises to *ca.* 25%, owing to more complete breakdown of acetaldehyde, and, to a lesser extent, of propene (*cf.* Hurd, *op. cit.*, pp. 236 and 77, respectively).

Pyrolyses 8 and 9 (vessel P.1). These two runs show that reasonably reproducible results can be obtained (Table 3). The two liquid pyrolysates (a) were combined; distillation yielded (i) a volatile fraction, b. p. 20°/660 mm. (mainly acetaldehyde), (ii) a colourless liquid, b. p. 52—60°/760 mm. (mainly acetone), (iii) a yellowish liquid, b. p. 62—87°/760 mm. [mainly recovered (IX), *ca.* 22% of weight pyrolysed: unsaturated; polymerised on heating with benzoyl peroxide], and (iv) a cloudy yellow liquid, b. p. 97—114°/760 mm. (mainly acetic acid containing some acetic anhydride: infrared spectrum). The exit gases contained keten (acetanilide from aniline-ether trap), ethylene, propene, and acetylene (infrared spectrum), but no divinyl ether (infrared spectrum).

Pyrolyses 10 and 11 (vessel S). These duplicate runs again show reasonable reproducibility (Table 3). The liquid pyrolysates (a) contained traces of water (anhydrous CuSO_4 test); keten was absent from the gaseous pyrolysates (b).

Pyrolysis 12 (vessel V). Qualitatively, the results were the same as those of runs 8 and 9, but the ratio between the reaction routes was somewhat altered (Table 4). High accuracy is not claimed for the ratios summarised in Table 4, since certain products (*e.g.*, ethylene) cannot yet be accounted for; but approximate figures have been reached by correlating the analyses of gas (b) with the weight of the fractions obtained from liquid (a).

Vinyl isobutyrate (IX; R = R' = Me). The ester, prepared from vinyl acetate and isobutyric acid by ester interchange (*cf.* Burnett and Wright, *Trans. Faraday Soc.*, 1953, 49, 1108), had b. p. $105^\circ/760$ mm. It was briefly described in B.P. 585,396/1947 and U.S.P. 2,460,105/1949, but no physical constants were quoted.

Pyrolysis 13 (vessel P.3). The smallest reaction vessel was used because of the small quantity of ester available; and the entire liquid pyrolysate was collected directly in the cold trap. Distillation of (a) yielded (i) a volatile fraction, b. p. $20^\circ/660$ mm. (mainly acetaldehyde), (ii) a

TABLE 4. Ratios between reaction routes in pyrolysis of vinyl acetate and isobutyrate (Temp. 550°).

Pyrolysis No.	Reaction vessel	Ester	Route-ratio (molar)			
			A ²	B ¹	C ²	R/C ¹
8-9 (av.)	P.1	Acetate	0.03	0.47	0.03	0.47
12	V	"	0.11	0.15	0.01	0.73
13	P.3	isoButyrate	0.06	0.30	0.01	0.63

colourless liquid, b. p. $92-100^\circ/760$ mm. (mainly methyl isopropyl ketone), (iii) a colourless liquid, b. p. $102-108^\circ/760$ mm. [mainly unchanged (IX), *ca.* 7% of weight pyrolysed: infrared spectrum], and (iv) a brownish liquid, b. p. $145-165^\circ/760$ mm. (mainly isobutyric acid, containing no isobutyric anhydride: infrared spectrum). In addition to the three main components of the gaseous pyrolysate (b) listed in Table 3, the following three components were identified by the infrared spectrum: 2:3-dimethylbut-2-ene [bands at 1450 (s), 1390 (s), 1162 (s) cm^{-1}], 2-methylbut-1-ene [892 (w) cm^{-1}], and 2-methylbut-2-ene [804 (s) cm^{-1}]. 3-Methylbut-1-ene could not be identified positively.

New Infrared Data.—The gaseous pyrolysate (b) from runs 4, 8, 9, and 2 showed a strong band at 1140 cm^{-1} which still remains unassigned. The spectra of the following substances were measured, and do not appear to have been recorded previously: Benzoic anhydride [1787 (s), 1736 (m), 1620 (w), 1463 (w), 1210 (s), 1160 (m), 1035, 1010, 985 (triplet: s) cm^{-1}]; 1:3:5-tribenzoylbenzene [1652 (broad: s), 1555 (broad: s), 1239 (w) cm^{-1}]; vinyl isobutyrate [875 (w), 962 (w), 1103 (w), 1167 (m), 1209 (w), 1675 (w), 1795 (m) cm^{-1}]; vinyl benzoate [706 (w), 870 (w), 952 (w), 1028 (w), 1075 (m), 1100 (m), 1140 (s), 1260 (s), 1605 (w), 1650 (w), 1730 (m) cm^{-1}].

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