687. *Studies in Pyrolysis. Part VII.* Model Systems for the Pyrolysis of Poly(ethylene Terephthalate): 2 : 2'-Dibenzoyloxydiethyl Ether, 2-Benzoyloxyethyl Vinyl Ether, and Certain Related Vinyl Ethers.*

By H. V. R. IENGAR and P. D. RITCHIE.

In a vapour-phase flow-reaction vessel (*ca.* 450—500°), 2 : 2'-dibenzoyloxydiethyl ether yields a complex pyrolysate best explained by the following reaction sequence. Stage 1: Alkyl–oxygen scission at an ester group, yielding 2-benzoyloxyethyl vinyl ether and benzoic acid. Stage 2: Secondary breakdown of 2-benzoyloxyethyl vinyl ether by three competitive routes, (i) alkyl–oxygen scission at the ether group, yielding vinyl benzoate and acetaldehyde, (ii) disproportionation to ethylene dibenzoate and 1 : 2-divinyloxyethane, and (iii) alkyl–oxygen scission at the ester group, yielding benzoic acid and vinyl ether. Stage 3: A series of tertiary breakdowns of the primary and secondary products. These conclusions are supported by the pyrolysis of divinyl, *n*-butyl vinyl, and *iso*butyl vinyl ethers. The bearing of the results on the pyrolysis of technical poly(ethylene terephthalate) is discussed.

ETHYLENE DIBENZOATE and vinyl benzoate have been used in previous studies [1,2] on the pyrolysis of poly(ethylene terephthalate), as model systems to represent the behaviour of a typical segment (Ia) in the polyester chain. Since it is known that occasional ether linkages (*e.g.*, diethylene glycol units) are unavoidably incorporated into the chain during polycondensation, the work has now been extended to an analogous pair of models, 2 : 2'-dibenzoyloxydiethyl ether (II) and 2-benzoyloxyethyl vinyl ether (III), to represent the behaviour of a chain segment (Ib).

The ether-diester (II), which is stable up to *ca.* 350° in a vapour-phase flow-reaction

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* Part VI, *J.*, 1956, 2628.

[1] Allan and Ritchie, *Chem. and Ind.*, 1953, 747.

[2] Allan, Forman, and Ritchie, *J.*, 1955, 2717.

vessel breaks down at *ca.* 450—500° to an extremely complex pyrolysate containing some fourteen constituents. It is possible to formulate more than one reaction scheme to account for these; but the following sequence, based on a correlation of the present results

$$\sim\mathrm{C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4}\sim \underset{\text{(Ia)}}{} \qquad \sim\mathrm{C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4}\sim \underset{\text{(Ib)}}{}$$

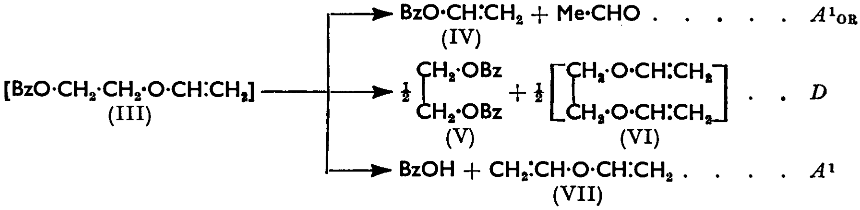
$$\underset{\text{(II)}}{\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OBz}} \qquad \underset{\text{(III)}}{\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH{:}CH_2}}$$

with other known relevant pyrolyses, appears to offer the best interpretation of the breakdown.

Stage 1 : Alkyl–oxygen scission at one of the two (identical) ester groupings, thus :

$$\underset{\text{(II)}}{\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OBz}} \longrightarrow \underset{\text{(III)}}{[\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH{:}CH_2}]} + \mathrm{BzOH} \quad . \; . \; . \quad A^1$$

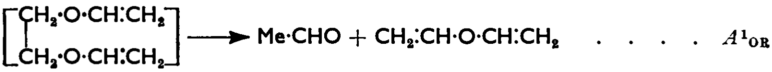
Stage 2 : Secondary breakdown of the relatively unstable ether-ester (III) by three competitive routes :



$$\underset{\text{(III)}}{[\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH{:}CH_2}]} \longrightarrow \begin{cases} \longrightarrow \underset{\text{(IV)}}{\mathrm{BzO{\cdot}CH{:}CH_2}} + \mathrm{Me{\cdot}CHO} \quad . \; . \; . \; . \; . \quad A^1{}_{\mathrm{OR}}\,\dagger \\ \longrightarrow \tfrac{1}{2}\underset{\text{(V)}}{\begin{bmatrix}\mathrm{CH_2{\cdot}OBz} \\ \mathrm{CH_2{\cdot}OBz}\end{bmatrix}} + \tfrac{1}{2}\underset{\text{(VI)}}{\left[\begin{matrix}\mathrm{CH_2{\cdot}O{\cdot}CH{:}CH_2} \\ \mathrm{CH_2{\cdot}O{\cdot}CH{:}CH_2}\end{matrix}\right]} \quad . \; . \quad D \\ \longrightarrow \mathrm{BzOH} + \underset{\text{(VII)}}{\mathrm{CH_2{:}CH{\cdot}O{\cdot}CH{:}CH_2}} \quad . \; . \; . \; . \quad A^1 \end{cases}$$

† For meaning of symbols, see Discussion.

Stage 3 : A series of tertiary breakdowns (i) of vinyl benzoate (IV), by the three competitive routes (A^2, C^2, R/C^1) noted by Allan, Forman, and Ritchie,[2] (ii) of ethylene dibenzoate (V), by the A^1 and D routes,[2] (iii) of acetaldehyde, by decarbonylation, (iv) of benzoic acid, by decarboxylation, and (v) of the unstable diether (VI), by the following consecutive routes :



(VI)

$$\left[\begin{matrix}\mathrm{CH_2{\cdot}O{\cdot}CH{:}CH_2} \\ \mathrm{CH_2{\cdot}O{\cdot}CH{:}CH_2}\end{matrix}\right] \longrightarrow \mathrm{Me{\cdot}CHO} + \mathrm{CH_2{:}CH{\cdot}O{\cdot}CH{:}CH_2} \quad . \; . \; . \; . \quad A^1{}_{\mathrm{OR}}$$

$$\underset{\text{(VII)}}{\mathrm{CH_2{:}CH{\cdot}O{\cdot}CH{:}CH_2}} \longrightarrow \mathrm{Me{\cdot}CHO} + \mathrm{CH{:}CH} \quad . \; . \; . \; . \; . \; . \; . \; . \quad A^2{}_{\mathrm{OR}}$$

The postulated relatively unstable intermediates (III) and (VI) were not identified directly; but (III) and the ether (VII) have been pyrolysed separately, with results in accord with the overall three-stage scheme. All the other products required by the scheme were identified, either chemically or by infrared spectrometry—carbon monoxide and dioxide, acetaldehyde, methane, benzoic acid and anhydride, benzene, vinyl benzoate, styrene, acetophenone, ethylene dibenzoate, vinyl ether, and acetylene (together with ethylene, the origin of which is not certain).

It is certain that free-radical mechanisms operate in at least some of the stages of this complex sequence of high-temperature reactions. The fact that the changes are formulated here, for simplicity, as molecular reactions is not intended to imply the absence of radical mechanisms; indeed, it is difficult to account for the formation of ethylene on any other basis.

DISCUSSION

To interpret more clearly the pyrolysis of the ether-esters studied, it is first necessary to survey briefly the pyrolysis of ethers in general.

Saturated Aliphatic Ethers.—A simple ether breaks down by a primary alkyl–oxygen scission :[3]

$$>CH{\cdot}O{\cdot}CH< \longrightarrow >CO + CH_2< \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad A^1{}_{\mathrm{R}}$$

The suffix R indicates that hydrogen is transferred across the point of scission to the hydrocarbon group R of an ether R–O–R. Transfer in the opposite sense, to the alkoxyl grouping OR ($A^1{}_{\mathrm{OR}}$ scission), is not observed.

Alkyl Vinyl Ethers.—In addition to the type of rearrangement discussed later, two initial types of scission are here formally possible, *viz.*, alkyl–oxygen (A^1) and alkenyl–oxygen (A^2), each with two possible alternative variations, thus :

$$CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH_2R \longrightarrow [CH_2{:}CH{\cdot}OH] + CH_2{:}CHR \quad . \; . \; . \; . \; . \quad A^1{}_{\mathrm{OR}}$$

$$\textit{or} \qquad \longrightarrow CH_2{:}CO + CH_3{\cdot}CH_2R \quad . \; . \; . \; . \; . \; . \quad A^1{}_{\mathrm{R}}$$

$$\textit{or} \qquad \longrightarrow CH{:}CH + CH_2R{\cdot}CH_2{\cdot}OH \quad . \; . \; . \; . \; . \quad A^2{}_{\mathrm{OR}}$$

$$\textit{or} \qquad \longrightarrow CH_2{:}CH_2 + CH_2R{\cdot}CHO \quad . \; . \; . \; . \; . \; . \quad A^2{}_{\mathrm{R}}$$

Wang and Winkler[4] found that ethyl vinyl ether yields acetaldehyde and ethylene (first-order reaction : *ca.* 380—450°) ; but here, since R = H, the evidence does not discriminate between routes $A^1{}_{\mathrm{OR}}$ and $A^2{}_{\mathrm{R}}$, both of which would yield the same pair of primary products. It is now shown that $A^1{}_{\mathrm{OR}}$ is the favoured route for alkyl vinyl ethers, since the two butyl vinyl ethers (VIII) and (IX) both yield acetaldehyde and a butene smoothly at *ca.* 500°, with no evidence for formation of a butyraldehyde and ethylene by route $A^2{}_{\mathrm{R}}$; neither is there evidence for routes $A^1{}_{\mathrm{R}}$ or $A^2{}_{\mathrm{OR}}$.

$$\underset{\text{(VIII)}}{CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH_2Et} \longrightarrow Me{\cdot}CHO + CH_2{:}CHEt \quad . \; . \; . \; . \; . \quad A^1{}_{\mathrm{OR}}$$

$$\underset{\text{(IX)}}{CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CHMe_2} \longrightarrow Me{\cdot}CHO + CH_2{:}CMe_2 \quad . \; . \; . \; . \; . \quad A^1{}_{\mathrm{OR}}$$

On the other hand, Hasche and Thompson[5] have reported that alkyl vinyl ethers ($CH_2{:}CH{\cdot}O{\cdot}R$), over a wide range of temperatures and pressures, rearrange to isomeric aldehydes ($R{\cdot}CH_2{\cdot}CHO$). Pyrolysis of the butyl vinyl ethers (VIII) and (IX) produced neither C_6-aldehydes nor the pentanes which these should yield on decarbonylation; nevertheless, some ethers exhibiting 1 : 2-unsaturation, such as allyl vinyl ether, certainly rearrange thermally in this way.[6, 7]

Vinyl ether (VII), being fully symmetrical and unsaturated, presents a special case. Taylor[8] concluded that this ether breaks down (sealed tube : *ca.* 450°) by a complex series of free-radical reactions, and that the major scission-route is :

$$\text{(VII)} \quad CH_2{:}CH{\cdot}O{\cdot}CH{:}CH_2 \longrightarrow CH_2{:}CO + CH_2{:}CH_2 \quad . \; . \; . \; . \; . \; . \; . \quad A^2{}_{\mathrm{R}}$$

However, in the flow vessel now employed (*ca.* 500°), breakdown occurs by the following $A^2{}_{\mathrm{OR}}$ route, with no evidence for rearrangement :

$$\text{(VII)} \quad CH_2{:}CH{\cdot}O{\cdot}CH{:}CH_2 \longrightarrow Me{\cdot}CHO + CH{:}CH \quad . \; . \; . \; . \; . \; . \quad A^2{}_{\mathrm{OR}}$$

In the light of these considerations, the present pyrolyses can now be more critically interpreted.

Competitive Ether- and Ester-scissions.—The primary breakdown of ether-diester (II) by alkyl–oxygen scission at an ester grouping, rather than at the ether grouping (Stage 1), is supported by a number of analogies. For example, ethyl carboxylates in general show A^1 scission well below 500°, whereas ethyl ether is stable[3] at *ca.* 500° though it undergoes $A^1{}_{\mathrm{R}}$ scission at *ca.* 550°. This thermal selectivity is confirmed by the complete absence

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[3] Hurd, " The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chap. 8.

[4] Wang and Winkler, *Canad. J. Res.*, 1943, **21**, *B*, 97.

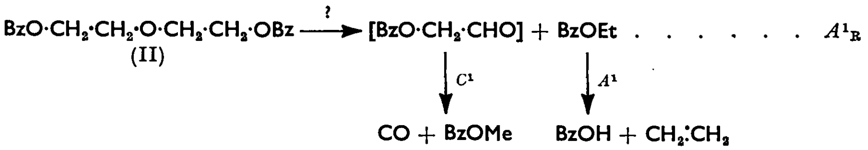
[5] Hasche and Thompson, U.S.P. 2,294,402/1942.

[6] Claisen, *Ber.*, 1896, **29**, 2932.

[7] Hurd and Pollack, *J. Amer. Chem. Soc.*, 1938, **60**, 1905.

[8] Taylor, *J. Chem. Phys.*, 1936, **4**, 116.

of methyl benzoate from the pyrolysate from (II); for, if the ether grouping provided a point of scission, it should be possible to detect end-products from the following predictable sequence :

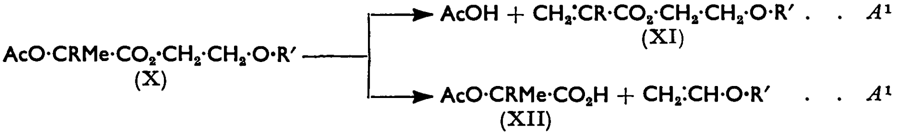


$$\begin{tikzcd}
\underset{\text{(II)}}{\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OBz}} \arrow[r, "?"] & {[\mathrm{BzO{\cdot}CH_2{\cdot}CHO}]} \arrow[d, "C^1"] & + \ \mathrm{BzOEt} \arrow[d, "A^1"] & \ldots\ldots\ A^1_R \\
& \mathrm{CO + BzOMe} & \mathrm{BzOH + CH_2{:}CH_2} &
\end{tikzcd}$$

Ethyl benzoate should be largely destroyed at *ca.* 500°, and ethylene is, in fact, obtained on pyrolysis of both (II) and (III); but, since vinyl benzoate (IV) is also formed in each case, and since it is known [2] that on pyrolysis this vinyl ester yields ethylene (*inter alia*) by some unknown route, formation of the olefin cannot here be taken, by itself, as evidence for ethyl benzoate as its precursor. However, methyl benzoate is a very thermostable ester; [9] its complete absence therefore indicates A^1 scission of (II) at an ester grouping as the sole primary breakdown route at *ca.* 450—500°.

This same evidence indicates that the ether-ester (III) does not break down by A^2_R scission to ethylene and the unstable benzoyloxyacetaldehyde. This agrees with the known pyrolysis of alkyl vinyl ethers such as (VIII) and (IX); but it would be expected that pyrolysis of (III) should occur by the A^1_{OR} scission characteristic of such ethers, in competition with A^1 scission of the ester grouping, and the overall breakdown of (III) is best interpreted as a competition between A^1_{OR}, D, and A^1 routes (Stage 2). The disproportionation route is proved by the occurrence of ethylene dibenzoate (V) (see below), though the evidence for the two alkyl–oxygen scissions (A^1_{OR} and A^1) is less direct. Mere identification of vinyl benzoate and acetaldehyde in the pyrolysate from (III) does not of itself prove an A^1_{OR} scission or identification of benzoic acid and vinyl ether an A^1 scission, since these four products could also arise by further breakdown (Stage 3) of the products from the D route. However, the A^1_{OR} route is strongly supported by the known breakdown of alkyl vinyl ethers, and the A^1 route by the fact that vinyl ether (VII) was identified in one run at *ca.* 470° in which no ethylene dibenzoate was detected. This slight variation between the results of two similar runs may be due to different degrees of carbonisation at the wall of the reactor, or to unintentional variations in feed rate or temperature.

The conclusion that primary breakdown of the ether-diester (II) occurs by an A^1 scission agrees well with the known pyrolysis (*ca.* 450—500°) of certain ether-diesters (X) in which the presence of two dissimilar ester groupings offers the formal possibility of two competing A^1 scissions, thus :



$$\begin{tikzcd}
& \underset{\text{(XI)}}{\mathrm{AcOH + CH_2{:}CR{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}R'}} \quad \ldots\ A^1 \\
\underset{\text{(X)}}{\mathrm{AcO{\cdot}CRMe{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}R'}} \arrow[ur] \arrow[dr] & \\
& \underset{\text{(XII)}}{\mathrm{AcO{\cdot}CRMe{\cdot}CO_2H}} + \mathrm{CH_2{:}CH{\cdot}O{\cdot}R'} \quad \ldots\ A^1
\end{tikzcd}$$

Burns, Jones, and Ritchie [10] found that the esters (X; R = Me, R′ = Me or Ph) follow the first of these routes, giving α-methylacrylates (XI; R = Me) in yields up to at least 76%. Similarly, Fein, Ratchford, and Fisher [11] found that the esters (X; R = H, R′ = Me, Et, Bu^n, or tetrahydrofurfuryl) produce acrylates (XI; R = H) by the first route; but here the yield is generally low. This poor yield may be due to secondary breakdown of the primary products; alternatively, or in addition, there may be competitive primary scissions—either an A^1_R breakdown of the original ether grouping ($-\mathrm{CH_2{\cdot}CH_2{\cdot}O{\cdot}R'}$), or formation of the acid (XII) and an alkyl vinyl ether by way of the second A^1 route. No such ethers were, in fact, observed; but their known breakdown-product, acetaldehyde, was noted by Fein *et al.*[11] in the pyrolysates from the methoxy- and ethoxy-esters.

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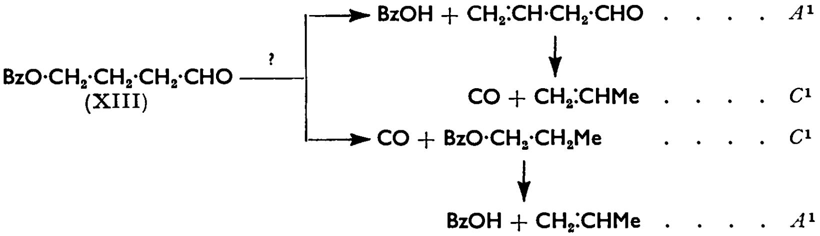
[9] Engler and Low, *Ber.*, 1893, **26**, 1440.

[10] Burns, Jones, and Ritchie, *J.*, 1935, 714.

[11] Fein, Ratchford, and Fisher, *J. Amer. Chem. Soc.*, **1944**, **66**, 1201.

Another probable source of this aldehyde is the known thermal breakdown [12] of α-acetoxypropionic acid (XII; R = H). There is, therefore, direct evidence for the first A^1 scission, and indirect evidence for competition by the second: there is no positive evidence for primary scission at the original ether grouping, though the unspecified gaseous hydrocarbons reported by Fein *et al.*[11] may have included products indicative of a minor scission at this point.

Rearrangement of Vinyl Ethers.—The vinyl ethers (VII), (VIII), and (IX) show no pyrolytic rearrangement; and the pyrolysis of ether-ester (III) is consistent with this, there being evidence of competitive scissions (A^1 and A^1_{OR}) and disproportionation (D) only. If rearrangement (R) to γ-benzoyloxybutyraldehyde (XIII) also competed to any measurable extent, it should be possible to detect end-products from the following predictable sequence:



There was, however, no sign of propene or its immediate precursors, though all were carefully sought by infrared spectrometry.

Disproportionation.—Ethylene dibenzoate (V) is present in the pyrolysates from the ether-diester (II: *ca.* 450°) and from the ether-ester (III: *ca.* 470°), though at higher temperatures it is destroyed, as might be predicted from earlier results.[2] Its formation can be readily explained only by assuming a disproportionation of the ether-ester (III), the accompanying product being the diether (VI). The latter substance was not identified, probably owing to the relatively easy pyrolysis of vinyl ethers in general; but its predictable scission-products, acetaldehyde and vinyl ether (VII), were identified. The latter survived the temperature of the reaction vessel in small amount only, and was detected by infrared spectrometry, though its known secondary scission-products, acetaldehyde and acetylene, were readily observed. In view of Taylor's results,[8] keten was carefully sought, since it is a formally possible breakdown-product of the vinyl ethers (III) and (VI) by A^1_R and of (VII) by A^2_R scission; but no evidence for this product could be found.

Origin of Acetylene.—This substance is attributed to two sources—the observed A^2_{OR} scission of vinyl ether (VII), and the already known alkenyl–oxygen scission (A^2) of vinyl benzoate (IV).[2] Two other formally possible sources can be eliminated—A^2_{OR} scission of the vinyl ethers (III) and (VI). If the former breaks down in this way, the accompanying primary product should be 2-hydroxyethyl benzoate (XIV), thus:

$$\underset{\text{(III)}}{\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH{:}CH_2}} \xrightarrow{?} \underset{\text{(XIV)}}{\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}OH}} + \mathrm{CH{:}CH} \quad . \ . \ . \ . \quad A^2_{OR}$$

However, the hydroxy-ester (XIV) yields water (*inter alia*) on pyrolysis; [13] and water was not observed in any of the present pyrolysates, though carefully sought. If, on the other hand, acetylene arose by A^2_{OR} scission of the diether (VI), the accompanying primary product should be 2-hydroxyethyl vinyl ether (XV), a substance which is very readily cyclised to the acetal (XVI).[14] Hurd and Botterton,[15] in an attempt to prepare the

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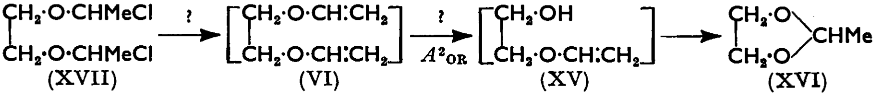
[12] Bagard, *Bull. Soc. chim. France*, 1907, **1**, 307.

[13] Cretcher and Pittenger, *J. Amer. Chem. Soc.*, 1925, **47**, 2560.

[14] Hill and Pidgeon, *ibid.*, 1928, **50**, 2718.

[15] Hurd and Botterton, *ibid.*, 1946, **68**, 1200.

diether (VI) by dehydrochlorinating the chlorinated diether (XVII), unexpectedly obtained the cyclic acetal instead; and this suggests the following possible sequence of reactions :



It appears, however, that another explanation must be sought for Hurd and Botterton's result, since a repetition of their experiment has shown no liberation of acetylene. This fact, coupled with the failure of the butyl vinyl ethers (VIII) and (IX) to yield acetylene on pyrolysis, strongly argues against $A^2{}_{\mathrm{OR}}$ scissions of either (III) or (VI) as a source of the observed acetylene.

Application of the Results to Polyesters.—Pohl [16] has shown that poly(ethylene terephthalate) is more thermostable than the polycondensate from terephthalic acid and diethylene glycol, for which the ether-diester (II) now provides an ideal model system. Pohl used, as an index of breakdown, the volume of gas evolved under standard conditions; and the present work shows that complete breakdown of a diethylene glycol unit (Ib) would, in fact, give a much larger volume of gas than that of an ethylene glycol unit (Ia). Further, it is clear that acetaldehyde, a recognised major breakdown-product of commercial " Terylene " or " Dacron," can arise not only from the predominating chain-segments such as (Ia),[2] but also from occasional segments such as (Ib) which are unavoidably present to some extent in the polyester chain.

Pohl worked with molten polyesters, whereas the present studies cover vapour-phase pyrolyses. Caution is clearly required in correlating the results; but experiments which will be described in a future communication show that the correlation is permissible for this groups of compounds.

EXPERIMENTAL

Apparatus.—Pyrex-glass flow-reaction vessels of the type previously described [2] were used, with the same system for collecting pyrolysate fractions, and with temperatures automatically controlled to within ±5°. Before each run the whole system was flushed with nitrogen, to avoid oxidation of the heated vapour.

Analytical Methods.—Aldehydes and ketones were characterised as their 2 : 4-dinitrophenylhydrazones (mixed m. p. or, where specified, paper chromatography [17]). All other solid products were identified by mixed m. p. Keten was sought in gaseous pyrolysates by means of the usual aniline trap. The normal chemical examination of pyrolysate fractions was in many cases supplemented by infrared spectrometry.

The Table summarises the experimental conditions for 9 runs. It shows the amount (*a*) of liquid pyrolysate (excluding minor amounts of volatile materials condensed in the cold trap, cooled in solid carbon dioxide) and also the amount (*b*) and composition of the final exit-gases. All gas analyses are reported on a nitrogen-free basis.

2 : *2′-Dibenzoyloxydiethyl Ether* (II).—*Preparation* (*A*). Dry sodium benzoate (50 g.), 2 : 2′-dichlorodiethyl ether (100 g.), and a few drops of diethylamine, heated at 200° for 6 hr., yielded 2-benzoyloxyethyl 2-chloroethyl ether, b. p. 166°/8 mm. (lit.,[18] 191°/25 mm.) (Found : C, 58·1; H, 6·0. Calc. for $C_{11}H_{13}O_3Cl$: C, 57·8; H, 5·7%), and the ether-diester (II) (10 g., 18%), m. p. 33·5°, b. p. 250°/3 mm. (lit.,[18] b. p. 279—281°/24 mm.; no m. p. recorded previously).

Preparation (*B*). 2 : 2′-Dihydroxydiethyl ether (diethylene glycol), on benzoylation (Schotten–Baumann), yielded the ether-diester (II) (47%) (Found: C, 68·6; H, 6·0. Calc. for $C_{18}H_{18}O_5$: C, 68·8; H, 5·7%).

Pyrolysis 1. Distillation of (*a*) yielded acetaldehyde, followed by (i) 6 g., b. p. 80—90° (mainly benzene, characterised as *m*-dinitrobenzene), (ii) 2·6 g., b. p. 90—120°, and (iii) 1·6 g., b. p. 120—160° (containing styrene; infrared). Benzoic acid was removed from the residue, by sodium hydrogen carbonate; further distillation then yielded (iv) 1·4 g., b. p. 160—210° (containing acetophenone), (v) 4 g., b. p. 210—280°, and (vi) 8·5 g., high-boiling residue. The gaseous pyrolysate (*b*) contained carbon monoxide and dioxide, methane, ethylene, and

[16] Pohl, *J. Amer. Chem Soc.*, 1951, **73**, 5660.

[17] Burton, *Chem. and Ind.*, 1954, 576.

[18] Cretcher, Koch, and Pittenger, *J. Amer. Chem. Soc.*, 1925, **47**, 1175.

acetylene, but no propene (infrared). As in previous related pyrolyses,[2] the infrared spectrum of (*b*) showed a strong unallocated band at 1140 cm.$^{-1}$. Keten was absent.

Pyrolysis 2. Vinyl ether (VII) was identified in the cold trap (infrared). The total liquid pyrolysate (*a*) was refluxed for 1 hr. with 10% aqueous sodium hydroxide (100 ml.); distillation of the hydrolysate (water-bath) yielded no alcohols (xanthate colour test[19]). A control test with added methanol, under the same conditions, gave a positive result.

Pyrolysis of compounds (II), (III), (VII), (VIII), *and* (IX).

Pyrolysand	(II)	(II)	(II)	(III)	(III)	(III)	(VII)	(VIII)	(IX)
Pyrolysis No.	1	2	3	4	5	6	7	8	9
Temp.	550°	500°	450°	500°	470°	400°	500°	500°	500°
Feed-rate (g./min.)	0·30	0·54	0·70	0·53	0·53	0·44	0·34	0·30	0·34
Wt. pyrolysed (g.)	64·0	35·0	73·1	70·0	20·0	28·0	32·5	47·0	30·0
(*a*) Liquid pyrolysate (g.)	23·3 *	23·6 *	52·6 *	57·8 *	13·3 *	22·2 *	†	‡	‡
(*b*) Gaseous pyrolysate (l.)	16·0	7·5	9·7	8·0	3·1	3·1	9·0	5·7	4·0
Composition (%) of (*b*):									
CO	41·0	44·5	39·5	59 §	53 §	43·5	48·2	33·9	39·1
CO_2	25·5	22·3	16·5	19 §	22 §	30·9	Nil	Nil	Nil
CH_4	23·9	22·8	31·4	Nil	Nil	Nil	27·4	46·3	49·0
Unsat. hydrocarbons	9·6	10·4	12·6	22 §	25 §	25·6	24·4	19·8	11·9

* Excluding minor amounts of volatile material in cold trap.
† Large volatile fraction in cold trap not weighed.
‡ Acetaldehyde (removed in 2 : 4-dinitrophenylhydrazine trap) and olefin (in cold trap) not weighed.
§ Approximate.

Pyrolysis 3. The liquid pyrolysate (*a*) contained benzoic anhydride (colour reaction[20]); distillation of (*a*) then yielded 7·1 g., b. p. 190—240°, which contained ethylene dibenzoate.

2-*Benzoyloxyethyl Vinyl Ether* (III).—*Preparation.* Dry sodium benzoate (60 g.), 2-chloroethyl vinyl ether (200 g.), and triethylamine (3 g.) (found to be a better catalyst than diethylamine), when refluxed gently (24 hr.) and filtered, gave 70 g. (87%) of the ether-ester (III), b. p. 138—140°/15 mm. (lit.,[14] 133°/9 mm.).

Attempts to prepare the product (III) by dehydrochlorinating 2-benzoyloxyethyl 2-chloroethyl ether with pyridine, quinoline, or collidine were unsatisfactory.

Pyrolysis 4. The cold trap contained vinyl ether (VII) (infrared) and acetaldehyde. Distillation of the main liquid pyrolysate (*a*) yielded a fraction containing benzoic acid, but no ethylene dibenzoate (contrast Pyrolysis 5). The gaseous pyrolysate (*b*) contained carbon monoxide and dioxide, methane, ethylene, and acetylene, but no propene (infrared). Keten was absent (aniline trap).

Pyrolysis 5. The cold trap contained acetaldehyde and an unsaturated liquid (not positively identified, but probably vinyl ether). Distillation of (*a*) yielded benzoic acid and the following liquid fractions: (i) b. p. 20—60°, (ii) b. p. 60—130°, (iii) b. p. 130—160°, (iv) b. p. 100—110°/15 mm., (v) b. p. 110—140°/15 mm., and (vi) b. p. above 200°/15 mm. Fraction (iv) contained acetophenone (paper chromatography of 2 : 4-dinitrophenylhydrazone[17]); fraction (vi) consisted of ethylene dibenzoate.

Pyrolysis 6. The cold trap contained acetaldehyde. Distillation of (*a*) yielded 3·7 g., b. p. 94°/15 mm. (vinyl benzoate: infrared), a trace of benzoic acid, and unchanged (III).

Vinyl Ether (VII).—*Purification.* Vinyl ether (anæsthetic quality; from May and Baker Ltd.), freed from inhibitor by distillation, had b. p. 28—34°.

Pyrolysis 7. The liquid pyrolysate (*a*) consisted of unchanged vinyl ether (infrared) and acetaldehyde. Liquid (*a*) yielded an immediate precipitate of acetaldehyde 2 : 4-dinitrophenylhydrazone, whereas pure vinyl ether yields this substance only very slowly, as a result of gradual hydrolysis of the ether. The gaseous pyrolysate (*b*) contained carbon monoxide, methane, and acetylene, but no propene (infrared).

n-*Butyl Vinyl Ether* (VIII).—*Purification.* The ether (from L. Light & Co.) was carefully redistilled, and had b. p. 92—94°.

Pyrolysis 8. Acetaldehyde was identified as in Pyrolysis 7. The cold trap contained an olefinic liquid; treated with bromine, this yielded 1 : 2-dibromobutane, b. p. 162—167° (lit.,[21] 166°). The main liquid pyrolysate (*a*) had b. p. 92—97°, and was unchanged (VIII).

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[19] Feigl, "Spot Tests: Vol. II; Organic Applications," Elsevier, Amsterdam, 4th Edn., 1954, p. 130.
[20] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.
[21] Lépingle, *Bull. Soc. chim. France*, 1926, **39**, 741.

There was no evidence of keten (aniline trap), *n*-butyraldehyde, or any other break-down product.

iso*Butyl Vinyl Ether* (IX).—*Purification.* The ether (from L. Light & Co.), carefully redistilled, had b. p. 82°.

Pyrolysis 9. Acetaldehyde was identified as in Pyrolysis 7. The cold trap contained an olefinic liquid; treated with bromine, this yielded 1 : 2-dibromo*iso*butane (9 g.), b. p. 149°, n_D^{10} 1·513 (lit.,[22] b. p. 149—151°, n_D^{20} 1·512). The main liquid pyrolysate (*a*) had b. p. 83°, and was unchanged (IX). There was no evidence of keten (aniline trap), *iso*butyraldehyde, or any other breakdown product.

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TECHNICAL CHEMISTRY DEPARTMENT, ROYAL TECHNICAL COLLEGE,
GLASGOW, C.1.
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[22] Krestinsky, *Ber.*, 1922, **55**, 2757.