404. *Studies in Pyrolysis. Part IX.* The Pyrolysis of the Model Systems 2-Benzoyloxyethyl and 2-p-Chlorobenzoyloxyethyl Terephthalate, and of Poly(ethylene Terephthalate).*

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2-Benzoyloxyethyl and 2-*p*-chlorobenzoyloxyethyl terephthalate break down in the vapour phase (*ca.* 400—550°) by several competitive routes: (i) various alkyl–oxygen scissions (A^1), yielding benzoic (or *p*-chlorobenzoic) and terephthalic acid, and (ii) disproportionation (D), yielding ethylene dibenzoate (or di-*p*-chlorobenzoate). Secondary breakdowns also occur (R/C^1, A^1/D, A^2, and C^2), as predicted.[1-3] Pyrolysis of poly(ethylene terephthalate) (*ca.* 340—475°) yields end-products all of which are in accordance with the same sequence of reactions.

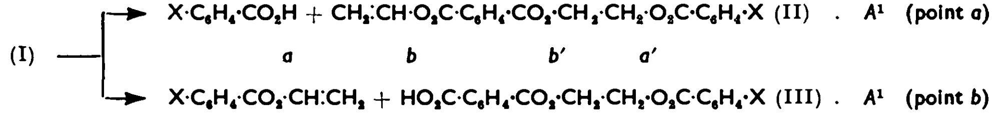
THE pyrolysis of various simple model compounds (*e.g.*, ethylene dibenzoate) has been used[1, 2, 4] as a basis for predicting in detail the thermal breakdown of poly(ethylene terephthalate). The predictions are now confirmed and extended by the pyrolysis (*ca.* 400—550°) of two larger models, 2-benzoyloxyethyl and 2-*p*-chlorobenzoyloxyethyl terephthalate (I; X = H and Cl respectively). As shown later, additional information can be obtained from the model in which the terminal aromatic rings are labelled by a chlorine atom. It is shown that all the breakdown products predicted by the use of such models can be identified in the pyrolysate (*ca.* 340—475°) from commercial poly(ethylene terephthalate).

(I)

$$p\text{-X}\cdot C_6H_4\cdot CO_2\underset{a}{\cdot}CH_2\cdot CH_2\underset{b}{\cdot}O_2C\cdot \underset{p}{C_6H_4}\cdot CO_2\underset{b'}{\cdot}CH_2\cdot CH_2\underset{a'}{\cdot}O_2C\cdot C_6H_4\cdot X\text{-}p$$

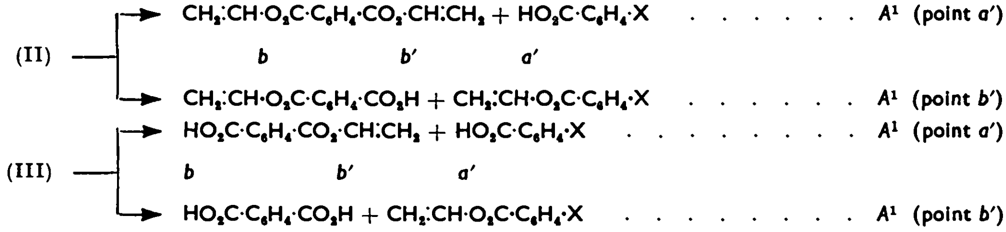
The following eleven products are formed from the diester (I; X = H or Cl) and the polyester itself: Benzoic and terephthalic acid, acetophenone, *p*-acetylbenzoic acid, acetaldehyde, acid anhydrides, carbon monoxide and dioxide, methane, ethylene, and acetylene. In addition, the diester (I; X = H) yields ethylene dibenzoate, vinyl benzoate, and benzene, while its chloro-derivative (I; X = Cl) also yields *p*-chlorobenzoic acid, *p*-chloroacetophenone, and ethylene di-*p*-chlorobenzoate.

The previous work of Allan, Forman, and Ritchie[2] provides an explanation for all these products. The ester (I) possesses two non-equivalent sets of β-hydrogen atoms; and the predominating primary breakdowns will be alkyl–oxygen scission (A^1) at points *a* or *b*, or at both competitively, thus:



$$(\text{I}) \longrightarrow \begin{cases} X\cdot C_6H_4\cdot CO_2H + CH_2{:}CH\cdot O_2C\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot O_2C\cdot C_6H_4\cdot X \text{ (II)} \quad . \quad A^1 \text{ (point } a) \\ \qquad\qquad a \qquad b \qquad b' \qquad a' \\ X\cdot C_6H_4\cdot CO_2\cdot CH{:}CH_2 + HO_2C\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot O_2C\cdot C_6H_4\cdot X \text{ (III)} \quad . \quad A^1 \text{ (point } b) \end{cases}$$

Thereafter, further alternative or competitive A^1 scissions of esters (II) and (III) can be predicted:



$$(\text{II}) \longrightarrow \begin{cases} CH_2{:}CH\cdot O_2C\cdot C_6H_4\cdot CO_2\cdot CH{:}CH_2 + HO_2C\cdot C_6H_4\cdot X \quad \dots\dots \quad A^1 \text{ (point } a') \\ \qquad b \qquad b' \qquad a' \\ CH_2{:}CH\cdot O_2C\cdot C_6H_4\cdot CO_2H + CH_2{:}CH\cdot O_2C\cdot C_6H_4\cdot X \quad \dots\dots \quad A^1 \text{ (point } b') \end{cases}$$

$$(\text{III}) \longrightarrow \begin{cases} HO_2C\cdot C_6H_4\cdot CO_2\cdot CH{:}CH_2 + HO_2C\cdot C_6H_4\cdot X \quad \dots\dots\dots \quad A^1 \text{ (point } a') \\ b \qquad b' \qquad a' \\ HO_2C\cdot C_6H_4\cdot CO_2H + CH_2{:}CH\cdot O_2C\cdot C_6H_4\cdot X \quad \dots\dots\dots \quad A^1 \text{ (point } b') \end{cases}$$

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* Part VIII, *J.*, 1957, 524.

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

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

[3] Allan, Jones, and Ritchie, *J.*, 1957, 524.

[4] Iengar and Ritchie, *J.*, 1956, 3563.

As each vinyl carboxylate is formed, it will undergo some measure of competitive breakdown by the R/C^1, A^2, and C^2 routes established previously;[2] for example, methyl ketones should be formed as end products, thus:

$$\begin{array}{rll} \mathrm{X{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH{:}CH_2} \longrightarrow & \mathrm{X{\cdot}C_6H_4{\cdot}COMe} & \ldots\ldots\ R/C^1 \\ \mathrm{HO_2C{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH{:}CH_2} \longrightarrow & \mathrm{HO_2C{\cdot}C_6H_4{\cdot}COMe} & \ldots\ldots\ R/C^1 \\ \mathrm{CH_2{:}CH{\cdot}O_2C{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH{:}CH_2} \longrightarrow & \mathrm{MeCO{\cdot}C_6H_4{\cdot}COMe} & \ldots\ldots\ 2(R/C^1) \end{array}$$

With the exception of the last product, *p*-diacetylbenzene (see Discussion), all the predicted end-products are observed on pyrolysis of the esters (I; X = H or Cl), and of poly(ethylene terephthalate) itself.

DISCUSSION

If compounds (I), (II), and (III) severally undergo, in fact, two competitive A^1 scissions, the overall breakdown scheme of the models is very complex. Almost every end-product can be accounted for in more than one way, and is therefore not diagnostic of a single route only. In practice the multiplicity of β-hydrogen atoms in each model virtually precludes a completely selective A^1 scission at each stage. Some of the alternative sources of particular products are discussed below, both for the model systems and for poly(ethylene terephthalate) itself.

Source of Benzoic Acid.—The ester (I; X = H) could formally yield benzoic acid either by A^1 scission at points *a*, *a′*, or by semidecarboxylation of the terephthalic acid produced by A^1 scission at *b*, *b′*. Since the ester (I; X = Cl) yields much *p*-chlorobenzoic acid and very little benzoic acid, it appears that semidecarboxylation of terephthalic acid is a very minor reaction in the pyrolysis of an ester (I).

Source of Ethylene Dibenzoate.—This compound may formally arise during pyrolysis of the ester (I; X = H) either by decarboxylation (C^2) of the acid (III; X = H) or by the following disproportionation (*D*) of the parent model by ester interchange:

$$2\,\mathrm{X{\cdot}C_6H_4{\cdot}[CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4]_{(m+n)/2}{\cdot}X} \longrightarrow \left\{ \begin{array}{c} \mathrm{X{\cdot}C_6H_4{\cdot}[CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4]_{m}{\cdot}X} \\ + \\ \mathrm{X{\cdot}C_6H_4{\cdot}[CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4]_{n}{\cdot}X} \end{array} \right. \quad . \quad D$$

For the model compound (I), $m + n = 4$, and the *D* products will have $m = 1$ (*i.e.*, ethylene dicarboxylate) and $n = 3$. The *D* process may continue further: for example, the larger of the two initial products may now be considered as having $m + n = 6$, and could yield two pairs of products, with $m = 1$, $n = 5$, and $m = 2$, $n = 4$. (It is doubtful whether the larger molecules produced in each *D* reaction will persist in the pyrolysate; they will tend to break down by A^1 scission.) Hence, whatever the degree of disproportionation of the ester (I; X = H), ethylene dibenzoate will be formed; but, since X = H, it is here impossible to discriminate between A^1/C^2 and *D* as the route leading to it. However, the model (I; X = Cl), in which the terminal aromatic rings are labelled by chlorine, yields the corresponding product ethylene di-*p*-chlorobenzoate but not ethylene dibenzoate; here, therefore, the former diester can have arisen from the parent model by the *D* route only. The absence of ethylene dibenzoate simultaneously rules out the alternative possibility that the di-*p*-chlorobenzoate might have arisen less directly from the acid (III; X = Cl) by successive C^2 and *D* reactions; furthermore, there was no sign of the acid (III; X = Cl), or of its decarboxylation product 2-benzoyloxyethyl *p*-chlorobenzoate.

It is clear from this result that a process of continual ester-interchange will proceed in molten poly(ethylene terephthalate) during its pyrolysis.

Source of Acid Anhydrides and Acetaldehyde.—It has been shown[3] that consecutive A^1

and *D* reactions are responsible for the formation of benzoic anhydride and acetaldehyde in the pyrolysis of ethylene dibenzoate :

$$\begin{aligned} \text{BzO·CH}_2\text{·CH}_2\text{·OBz} &\longrightarrow \text{BzOH} + \text{BzO·CH:CH}_2 \quad \ldots\ldots\ldots \quad A^1 \\ &\rightleftharpoons \text{BzO·CHMe·OBz} \\ &\longrightarrow \text{Bz}_2\text{O} + \text{Me·CHO} \quad \ldots\ldots\ldots \quad D \end{aligned}$$

Precisely the same A^1/D mechanism can explain the formation of acid anhydrides and acetaldehyde from (I), and also [5, 6] from poly(ethylene terephthalate). As random scission [5, 6] of the polyester chain proceeds, collision and interaction between carboxyl and vinyl ester end-groups will occur more frequently as the individual molecules become smaller and more mobile; and this mobility will be assisted by continual ester-interchange in the molten polyester. (There are, of course, other ways in which acetaldehyde can be formed on pyrolysis of the polyester.[4,7])

Source of Methyl Ketones.—Both for the model (I) and for poly(ethylene terephthalate), many of the vinyl ester end-groups formed by primary A^1 scission will be destroyed by the foregoing secondary A^1/D process : [3]

$$\sim\!\sim\text{C}_6\text{H}_4\text{·CO}_2\text{·CH:CH}_2 + \text{HO}_2\text{C·C}_6\text{H}_4\sim\!\sim \xrightarrow{-\text{Me·CHO}} \sim\!\sim\text{C}_6\text{H}_4\text{·CO·O·OC·C}_6\text{H}_4\sim\!\sim$$

Nevertheless, sufficient must survive long enough to allow the R/C^1 process to operate. The acetophenone produced from the ester (I; $X = H$) may formally arise both by R/C^1 breakdown of vinyl benzoate [1, 2] and by decarboxylation of the *p*-acetylbenzoic acid produced from vinyl hydrogen terephthalate by the R/C^1 reaction. However, the former route must predominate strongly because *p*-chloroacetophenone is present in much greater amount than acetophenone in the pyrolysate from the chloro-ester (I; $X = Cl$), and because *p*-acetylbenzoic acid, pyrolysed for as long as 10 min. at *ca.* 500° in the semimicro-apparatus described by Bain and Ritchie,[8] is decarboxylated to the extent of only *ca.* 25%.

If the competitive A^1 scissions of the polyester chain are truly random, as indicated by the work of Pohl [5] and of Marshall and Todd,[6] terephthalic acid and its mono- and di-vinyl ester should initially be formed in roughly equivalent amounts. Nevertheless, though the acid is a major product in the pyrolysis of both model (I) and the polyester itself, *p*-acetylbenzoic acid [expected to arise from the diester (I) *via* vinyl hydrogen terephthalate, by R/C^1 breakdown, and from the polymer by one or more predictable routes] is observed in small amounts only, and is detectable with difficulty; and *p*-diacetylbenzene [expected to arise from the diester (I) *via* vinyl terephthalate, by two successive R/C^1 changes, and from the polymer by similar predictable routes] could not be detected at all, though very carefully sought. Either, therefore, the diketone is produced in amounts too small to be detected (owing to predominating destruction of its precursor by the A^1/D reaction), or the R/C^1 breakdown of one vinyl ester group so modifies the electronic structure of the (unsymmetrical) product, vinyl *p*-acetylbenzoate, that the second vinyl ester group breaks down preferentially by one of the other competitive routes. The former explanation seems the more probable.

An interesting minor product has been obtained by fractionation of the pyrolysate (liquid phase; *ca.* 340°) from the polyester. It was too small in amount for rigorous purification; but all its chemical properties point to the constitution

$$\text{MeCO·C}_6\text{H}_4\text{·CO}_2\text{·CH}_2\text{·CH}_2\text{·O}_2\text{C·C}_6\text{H}_4\text{·CO}_2\text{H}$$

which is perfectly in accordance with the postulated overall scheme of decomposition.

All the model compounds used in this work have been pyrolysed in the vapour phase, and caution is required in applying the results to predict the breakdown of poly(ethylene

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

[6] Marshall and Todd, *Trans. Faraday Soc.*, 1953, **49**, 67.

[7] Iengar and Ritchie, unpublished observations, 1956.

[8] Bain and Ritchie, *J.*, 1955, 4407.

terephthalate) in the liquid phase. Nevertheless, the present results show that the predictions are justified. When the polyester is pyrolysed in the liquid phase (*ca.* 340°), all the products are explicable on the lines discussed; and there is a large residue of material which is still polymeric, though of reduced molecular weight and increased solubility in phenol. When, on the other hand, molten polyester is fed (at *ca.* 450—475°) into the vapour-phase reaction vessel used for the model compounds, so as to simulate vapour-phase conditions as nearly as possible, breakdown is almost complete, and all the predicted products (except *p*-diacetylbenzene) are observed.

EXPERIMENTAL

Apparatus.—The model compounds (I; X = H or Cl) were pyrolysed in the vapour-phase as previously described,[2] in reactors of various sizes giving a range of different contact times (see Table). Poly(ethylene terephthalate) was pyrolysed (i) by running the molten polyester into a vapour-phase reaction vessel, and also (ii) by heating it under nitrogen in a 3-necked Quickfit flask, enclosed in an electric heating mantle, and fitted with thermometer pocket, cold trap, and balanced aspirator for collecting the exit gases. *p*-Acetylbenzoic acid was pyrolysed in the semimicro-apparatus described previously.[8]

Analytical Methods: Results.—The Table summarises the chief experimental conditions for 8 pyrolyses. Gas analyses are reported on a nitrogen-free basis. Contact times are calculated as previously.[3]

Normal chemical examination of pyrolysate fractions (*a*) and (*b*) (Table) was frequently supplemented by infrared spectrometry and paper chromatography. Carbonyl compounds were identified as their 2 : 4-dinitrophenylhydrazones, either by mixed m. p. or by the paper-chromatographic technique described by Burton.[9] All other solid materials were identified by mixed m. p. Acid anhydrides were detected by the Davidson–Newman colour reaction.[10]

2-*Benzoyloxyethyl Terephthalate* (I; X = H).—*Preparation.* Sodium terephthalate and 2-chloroethyl benzoate (molar ratio 1 : 2) were heated under reflux with a little diethylamine (200°; 5 hr.; rapid stirring). The product, extracted with benzene and recrystallised from methanol–ethanol, yielded 2-*benzoyloxyethyl terephthalate* (31%) as colourles needles, m. p. 114—115° [Found: C, 67·7; H, 4·9%; *M* (cryoscopic in benzene), 471. $C_{26}H_{22}O_8$ requires C, 67·6; H, 4·8%; *M*, 462]. It shows major infrared absorption bands at *ca.* 1780 *s*, 1365 *m*, 1305 *s*, 1145 *s*, 1050 *w*, 996 *w*, 865 *w*, 840 *m*, and 702 *m* cm.$^{-1}$. This compound was also prepared independently and simultaneously in the Blackley Laboratories of Imperial Chemical Industries Limited, Dyestuffs Division.

Pyrolysis of esters (I; X = H *and* Cl) *and poly*(*ethylene terephthalate*).

Pyrolysand	(I; X = H)				(I; X = Cl)		Polyester	
Pyrolysis no.	1	2	3	4	5	6	7	8
Temp.	500°	500°	400°	500°	500°	525—550°	450—475°	340°
Feed rate (g./min.)	0·54	0·50	0·40	0·70	1·03	1·03	0·67	†
Contact time (sec.)	24	44	63	15	125	115	—	†
Wt. pyrolysed (g.)	66	100	50	50	65	51·5	50	100
(*a*) In cold trap (g.)	2	3	1	—	1	Nil *	5	5
(*b*) In main receiver (g.)	37	58	39	42·5	47	25	17	>84 ‡
(*c*) Gaseous pyrolysate (l.)	6	12·5	2	4·5	4	6·9	9	1
Composition (%) of (*c*):								
CO	—	53·4	48·7	53·3	65·6	54·0	45·6	70·5
CO_2	—	42·7	43·5	40·0	27·7	44·7	47·8	24·9
Sat. hydrocarbons	—	Nil	Nil	Nil	Nil	Nil	Trace	Nil
Unsat. hydrocarbons	—	3·9	7·8	6·7	6·7	1·3	6·6	4·6

* Acetaldehyde vapour removed by 2 : 4-dinitrophenylhydrazine trap before reaching cold trap. † Pyrolysed in static system (5 hr.). ‡ A little of the sublimate could not be scraped out of the vessel. Dashes (—) imply items not examined. Note: There were overall losses due to carbonisation in the reaction vessel.

Pyrolysis 1. The liquid (*a*) in the cold trap contained acetaldehyde; there was no keten (aniline–ether trap). The total pyrolysate was treated with ether; the insoluble residue

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

[10] Davidson and Newman, *J. Amer. Chem Soc.*, 1952, **74**, 1515.

contained unchanged ester (I; X = H) and terephthalic acid, and the ethereal solution gave benzoic acid (12 g.) by means of an alkaline wash.

The remaining ethereal solution, distilled, yielded (i) 4 g., b. p. 70—100°/2 mm., and (ii) 2 g., b. p. 116—160°/1 mm. Fraction (i) consisted of vinyl benzoate and acetophenone (infrared); these were also present (traces) in fraction (ii), along with benzoic acid. The reaction vessel contained much carbonised matter.

Pyrolysis 2. The liquid (*a*) in the cold trap contained benzene (characterised as *m*-dinitrobenzene) and acetaldehyde. Product (*b*) yielded (i) 5 g., b. p. 75—86°/4 mm., (ii) 4·5 g., b. p. 86—92°/2 mm., (iii) 15 g., b. p. 92—120°/2 mm., and (iv) a solid residue. Fractions (i)—(iii) were similar to the corresponding fractions from pyrolysis 1; fraction (iii) contained a little acetophenone; residue (iv) contained unchanged ester (I; X = H) and terephthalic acid, and on ether-extraction yielded ethylene dibenzoate. There was much carbonised matter.

Pyrolysis 3. The ester (I; X = H) employed was here recrystallised from benzene instead of ethanol–methanol, to ensure that any acetaldehyde formed came from the ester itself and not from any traces of residual alcohol. The liquid (*a*) was mainly acetaldehyde; product (*b*) yielded (i) 1 g., b. p. 100—114°/6 mm. (vinyl benzoate and acetophenone; infrared), and (ii) 1 g., b. p. 114—120°/6 mm. (benzoic acid). The distillation residue (*ca.* 37 g.) was shaken with ether and aqueous potassium carbonate, and filtered; the insoluble residue (14 g.) consisted of unchanged ester (I; X = H) and potassium terephthalate; the aqueous layer, acidified, yielded benzoic acid (14 g.) and terephthalic acid (1 g.); the ethereal layer, on evaporation, yielded a solid (9 g.) which on recrystallisation gave ethylene dibenzoate (mixed m. p.) and a residue containing benzoic anhydride (colour reaction [10]).

Pyrolysis 4. Product (*b*) was shaken with ether and filtered; a 2 : 4-dinitrophenylhydrazone, prepared from the ethereal extract, was examined chromatographically,[9] control "spots" of the 2 : 4-dinitrophenylhydrazones of acetophenone and *p*-acetylbenzoic acid being applied. Elution with acetone (20%) in light petroleum (b. p. 60—80°) resolved the "unknown" spot into two well-defined spots corresponding exactly in position to those from two controls. There was in addition a faint spot, midway between the other two; this did not correspond to any known carbonyl compound, but is presumably due to another of the possible methyl ketones from the pyrolysis. (Pyrolyses 1—3 gave no evidence for the presence of *p*-acetylbenzoic acid; this could be demonstrated only when the Burton method [9] was applied.)

2-Chloroethyl p-*Chlorobenzoate.—Preparation.* Ethylene chlorohydrin and *p*-chlorobenzoyl chloride (molar ratio 1 : 1), heated at 100° for 2 hr., yielded pure *ester* (77%), m. p. 40°, b. p. 145°/5 mm. (Found: C, 49·6; H, 3·9; Cl, 32·0. $C_9H_8O_2Cl_2$ requires C, 49·3; H, 3·7; Cl, 32·4%).

2-Hydroxyethyl Terephthalate.—Preparation. Sodium terephthalate and ethylene chlorohydrin (molar ratio 1 : 6) were heated under reflux with a little diethylamine (140°; 24 hr.). Sodium salts were filtered off; the filtrate slowly deposited the crude hydroxy-ester (13%), which yielded *2-hydroxyethyl terephthalate* as plates, m. p. 112°, from acetone (Found: C, 56·7; H, 5·6. $C_{12}H_{14}O_6$ requires C, 56·7; H, 5·5%). This compound was also prepared independently and simultaneously in the Blackley Laboratories of Imperial Chemical Industries Limited, Dyestuffs Division.

*2-*p-*Chlorobenzoyloxyethyl Terephthalate* (I; X = Cl).—*Preparation* (a). Sodium terephthalate and 2-chloroethyl *p*-chlorobenzoate (molar ratio 1 : 2·5) were heated under reflux (200°) with a little diethylamine for 6 hr., tetralin being added as a neutral diluent. The product was poured into water and extracted repeatedly with chloroform; removal of chloroform from the extract yielded tetralin with the crude chloro-ester (20%) in suspension. The latter, decolorised with Norit–methanol, yielded *2-*p-*chlorobenzoyloxyethyl terephthalate* as fine needles, m. p. 140°, from methanol (Found: C, 59·1; H, 4·1. $C_{26}H_{20}O_8Cl_2$ requires C, 58·8; H, 3·8%).

Preparation (b). 2-Hydroxyethyl terephthalate, *p*-chlorobenzoyl chloride, and pyridine (molar ratio 1 : 2 : 6) were warmed together; the product, poured into water, yielded the crude chloro-ester (*ca.* 100%) as a yellowish solid. This was filtered off and washed successively with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water; recrystallisation from ethanol yielded pure ester (I; X = Cl), with properties as above.

Pyrolysis 5. In this trial run, the pyrolysate contained *p*-chlorobenzoic acid, a neutral solid, acid anhydride (colour reaction [10]), and a little acetaldehyde. The total pyrolysate yielded a 2 : 4-dinitrophenylhydrazone, which when chromatographed (circular Whatman No. 3

paper) and developed with aqueous ethanol gave four rings, showing the presence of four carbonyl compounds other than acetaldehyde.

Pyrolysis 6. The cold trap (*a*) contained acetaldehyde. The total non-gaseous pyrolysate (*b*), triturated with alkali and extracted with ether, yielded (i) an ether extract, (ii) an insoluble solid (1 g.) from the interface, and (iii) an alkaline layer which on acidification yielded a pale yellow solid. The latter gave a 2 : 4-dinitrophenylhydrazone; when chromatographed,[9] this gave a spot corresponding precisely (control) to the derivative from *p*-acetylbenzoic acid. 5 g. of (iii), treated with chloroform, gave 1 g. of an insoluble mixture of *p*-chlorobenzoic and terephthalic acid (infrared); the chloroform extract yielded a mixture of benzoic and *p*-chlorobenzoic acid (chromatography). Extract (i) yielded a liquid (22·7 g.) which solidified overnight. A 5 g. sample of this was macerated with light petroleum (20 ml.; b. p. 80—100°) and then warmed with a further 20 ml. of the same solvent; an upper layer (decanted from a lower layer of insoluble oil) yielded, on cooling, ethylene di-*p*-chlorobenzoate (0·6 g.), as prismatic rods, m. p. 133—139° (from ethanol) (mixed m. p. and infrared). Extract (i) also yielded a bright red 2 : 4-dinitrophenylhydrazone; this was chromatographed [11] on bentonite–kieselguhr (4 : 1), development being first with chloroform and working up to acetone. The eluate was collected in 10 ml. samples, and the separation followed by plotting optical density (Spekker; blue filter) against fraction number. Five well-defined maxima were recorded. The first two corresponded (chromatography [9]) to acetophenone and *p*-chloroacetophenone respectively; the other three (lower R_F values) remain unattributed, but very probably correspond to methyl ketones of higher complexity and molecular weight (cf. pyrolysis 5).

Poly(*ethylene Terephthalate*).—Carefully dried "Terylene" flake was used. In a trial pyrolysis, 10—20 g. samples were heated for 2 hr. under nitrogen in conical flasks immersed in a Wood's-metal bath; no decomposition was observed below 190°, but at 210—220° a white acidic sublimate was formed.

Pyrolysis 7. The cold trap (*a*) contained acetaldehyde. Pyrolysate (*b*), which contained acid anhydride (colour test [10]), was refluxed with ether (100 ml.) and gave a residue (2 g.) of terephthalic acid (infrared). The ether extract, washed with water and with aqueous alkali, and then dried, yielded a yellow liquid (1 g.) containing traces of suspended solid; it was mainly vinyl benzoate (infrared) containing some acetophenone (chromatography [9]). The aqueous extracts, when acidified, gave a yellowish solid (10 g.); this yielded a fraction soluble in hot water (mostly benzoic acid, but yielding also a trace of a 2 : 4-dinitrophenylhydrazone), an ethanol-soluble fraction containing *p*-acetylbenzoic acid (chromatography [9]), and an insoluble residue of terephthalic acid (infrared). The gaseous pyrolysate (*c*) contained carbon monoxide and dioxide, methane, ethylene, and acetylene (infrared).

Pyrolysis 8. The cold trap (*a*) contained acetaldehyde (5 g.) and no vinyl ether (infrared); there was a solid sublimate (*ca.* 14 g.) and a dark intractable solid residue (70 g.). The sublimate was boiled with water (100 ml.); the filtrate yielded benzoic acid on cooling; the residue was warmed with ethanol (100 ml.), yielding an insoluble residue of terephthalic acid (infrared) and a filtrate. A portion of the latter gave a 2 : 4-dinitrophenylhydrazone which formed two spots (chromatography [9]), one unknown and one corresponding to acetophenone; the remainder, on concentration, yielded a white solid *A*, m. p. >360°, and a filtrate which gave the 2 : 4-dinitrophenylhydrazone of acetophenone only.

64 g. of the dark tarry residue from the reaction vessel were treated with boiling acetone (400 ml.), yielding (i) a filtrate and (ii) an acetone-insoluble residue, more soluble in phenol than was the original polyester. On hydrolysis, fraction (ii) yielded ethylene glycol (characterised as its dibenzoate) and crude terephthalic acid (infrared); quantitative saponification gave 87·9% of terephthalic acid (Calc. for repeat-unit $[CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}C_6H_4{\cdot}CO_2]$: 86·4%). It thus appears that fraction (ii) is essentially a lower poly(ethylene terephthalate), the slightly high acid-content probably indicating the presence of some random anhydride linkages. The soluble fraction from filtrate (i) was separated by cold alkali into two sub-fractions, terephthalic acid and a solid with m. p. >350°, apparently identical with *A*.

Substance *A* dissolved in hot (but not cold) caustic alkali or sodium hydrogen carbonate; back-titration gave the titration equivalent (E_t), and addition of excess of acid regenerated *A*. Complete alkaline hydrolysis measured the saponification equivalent (E_s) and liberated terephthalic acid and ethylene glycol; the latter was determined (G%) by the periodic acid method. Attempts to determine molecular weight by the Rast method in camphor gave

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[11] Elvidge and Whalley, *Chem. and Ind.*, 1955, 589.

erratic and unreliable results. The substance was contaminated by a trace of *p*-acetylbenzoic acid (paper chromatography [9]) which could not be removed from the very small sample available; the following analytical data cannot, therefore, be considered as rigorously accurate, but point fairly conclusively to the constitution (IV; X = Ac, *n* = 0), 2-*p*-acetylbenzoyloxyethyl hydrogen terephthalate.

(IV) $X\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot[O_2C\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2]_n\cdot O_2C\cdot C_6H_4\cdot CO_2H$

The analytical data were compared with figures calculated for 12 different variations of the above formula (X = H, CO_2H, Ac: *n* = 0, 1, 2, 3); but for no other case was there good agreement [Found: C, 63·9; H, 4·7%; E_t, 361·9; E_s, 121·6, 123·8; *G*, 17·1%. $C_{19}H_{16}O_7$ (IV; X = Ac, *n* = 0) requires C, 63·9; H, 4·5%; E_t, 356; E_s, 118·7; *G*, 17·4%]. Attempts to detect *p*-acetylbenzoic acid in the total hydrolysate from *A* are meaningless, since the ketonic acid is originally present as a trace impurity.

p-*Acetylbenzoic Acid.—Preparation.* The acid, prepared by standard methods,[12, 13] had m. p. 200° (lit.,[13] 200°,[14] 208°).

Pyrolysis of p-*Acetylbenzoic Acid.*—In a semimicro-apparatus [8] (500°; 10 min.) 0·3 g. of acid evolved a gaseous pyrolysate (CO, 17·6; CO_2, 82·4%) containing 10·5 ml. of carbon dioxide, indicating 25·6% of decarboxylation. Examined by the nitroprusside test [15] for methyl ketones, the liquid residue gave a much stronger reaction than the original acid itself (checked by control mixtures); the odour of acetophenone was apparent.

p-*Diacetylbenzene.—Preparation.* The diketone was prepared from *p*-ethylacetophenone; [16] treatment with a large excess of 2 : 4-dinitrophenylhydrazine yielded a product which, even after several recrystallisations (glacial acetic acid) gave on chromatography [9] two resolved spots, presumably corresponding to mono- and di-2 : 4-dinitrophenylhydrazones. The recrystallised but unresolved mixture was used in testing pyrolysates chromatographically for the presence of *p*-diacetylbenzene.

Ethylene Di-p-*chlorobenzoate.—Preparation.* Ethylene glycol and *p*-chlorobenzoyl chloride (molar ratio 1 : 1), warmed in pyridine, yielded the diester, m. p. 142—143°, from ethanol (lit.,[17] 140°) (Found: Cl, 20·5. Calc. for $C_{16}H_{12}O_4Cl_2$: Cl, 20·9%).

[*Added March 8th,* 1957.] Since this paper was written, it has come to our notice that the preparation of 2-hydroxyethyl terephthalate has previously been recorded.[18] It is described as having m. p. 109° (from water).

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