498.   *Studies in Pyrolysis. Part XVIII.*[1]   *Vinyl and Allyl Esters of the Chlorobenzoic Acids, and Some Related Substances.*

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The three isomeric vinyl chlorobenzoates all break down (at *ca.* 500°) by the three competing scissions previously established for vinyl benzoate (A^2, R/C^1, C^2).   In addition, a fourth minor reaction (probably B^2 scission) yields chlorobenzaldehyde.   Change of orientation occurs to a small extent during the decarboxylation (C^2).   All three esters yield some acetaldehyde on pyrolysis: its origin is described, and possible mechanisms for all the breakdown reactions are outlined.   Competitive routes in the pyrolysis of allyl *o*-chlorobenzoate are also described.

The onset (threshold) temperatures of the various competing routes have been measured, and are smoothly related to certain parameters of the parent acid.

PREVIOUS work on the pyrolysis of vinyl [2,3] and allyl [3] benzoate has been extended to the corresponding *o*-, *m*-, and *p*-chlorobenzoates.   The objectives were (i) to determine, by means of the halogen label, whether orientation alters during such thermal reactions as decarboxylation, and (ii) to relate the relative ease of the competing reactions to various parameters of the parent acid (*e.g.*, dissociation constant).

Pyrolysis of Vinyl o-, m-, *and* p-*Chlorobenzoate.*—In the vapour phase (*ca.* 500°) all these esters undergo the three competing primary reactions already recorded [2,3] for vinyl benzoate.   In addition, small amounts of the corresponding chlorobenzaldehyde are formed, presumably by acyl–oxygen scission (B^2), although the keten which should
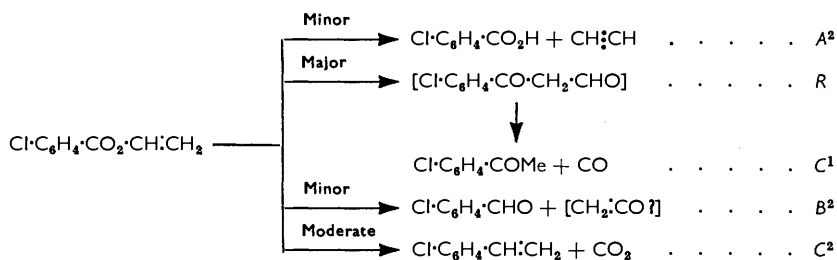
accompany the aldehyde in that reaction was not detectable.   There were also minor secondary products—chlorobenzene (from chlorobenzoic acid by C^2 scission, and possibly in part from chlorobenzaldehyde by C^1 scission); chlorotoluene (from chloroacetophenone by C^1 scission);   water (from dehydration [4] of free acid);   acid anhydride, acetaldehyde, and a non-volatile polymeric residue (origin discussed below).

Tables 1 and 2 summarise the composition of the complex pyrolysates (including, for comparison, results for vinyl benzoate).   Great accuracy is not claimed in Table 2.   Quantitative analysis is difficult, and the figures are based on a combination of several techniques.

Onset Temperatures of Competing Scissions.—When the temperature of a vinyl carboxylate is progressively raised, the competing breakdowns begin to operate one by one, each at a characteristic onset (or threshold) temperature $T(Z)$ at which some key-product Z, specific to the reaction in question, makes its first appearance.   This temperature is apparently a unique characteristic of the reaction, independent of the method and rate of

[1] Part XVII, Golomb and Ritchie, *J.*, 1962, 838.
[2] Allan, Forman, and Ritchie, *J.*, 1955, 2717.
[3] Allan, Jones, and Ritchie, *J.*, 1957, 524.
[4] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.

TABLE 1.

Composition (vol. %) of gaseous pyrolysate from $X \cdot C_6H_4 \cdot CO_2 \cdot CH\!:\!CH_2$ (after removal of acetaldehyde by a 2,4-dinitrophenylhydrazine trap).

| Product	X = o-Cl	m-Cl	p-Cl	H
CO	76·0	81·5	79·5	80·0
CO_2	17·5	9·0	13·0	14·0
Alkyne	3·5	7·0	5·5	3·0
Alkene	3·0	2·5	2·0	3·0
Sat. hydrocarbon	Trace	Trace	Trace	Trace

TABLE 2.

Composition (wt. %) of non-gaseous pyrolysate from $X \cdot C_6H_4 \cdot CO_2 \cdot CH\!:\!CH_2$ (removed from polymeric residue by distillation).

Product	X = o-Cl	m-Cl	p-Cl	H
$X \cdot C_6H_4 \cdot COMe$	59	55	58	54
$X \cdot C_6H_4 \cdot Me$	Trace	Trace	Trace	Trace
$X \cdot C_6H_4 \cdot CH\!:\!CH_2$	11	4	3	4
$X \cdot C_6H_4 \cdot CHO$	4	2	1	*
$X \cdot C_6H_4 \cdot CO_2H$	22	28	35	24
$X \cdot C_6H_5$	2	9	2	11
Acid anhydride	Trace	Trace	Trace	Trace
Unidentified	ca. 2	ca. 2	ca. 1	ca. 7

* Not identified in the present series of experiments, but later detected [5] as a trace.

measurement. A slower reaction does not occur at a lower temperature; control experiments in which an ester was held for a long period slightly below the measured onset temperature gave no sign of breakdown (cf. analogous results for alkyl triphenylacetates [6]).

When onset temperatures are plotted (see Figure) against the dissociation constant K
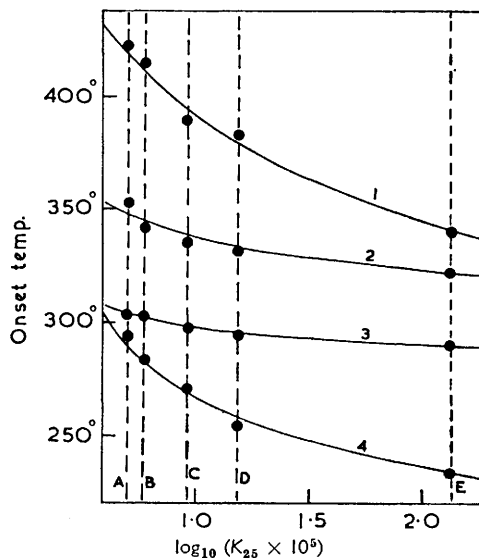
Relation between onset temperature for competing scissions of $X \cdot C_6H_4 \cdot CO_2 \cdot CH\!:\!CH_2$ and the dissociation constant of the parent acid $X \cdot C_6H_4 \cdot CO_2H$ [values of K_{25} from Ostwald (*Z. phys. Chem.*, 1889, **3**, 246, 255, 256, 270)]. Comparative data for vinyl *p*-toluate (X = *p*-Me) are included.

1, T(CH:CH). 2, T(CO). 3, T(CO_2). 4, T(Me·CHO).

A, X = *p*-Me. B, X = H. C, X = *p*-Cl. D, X = *m*-Cl. E, X = *o*-Cl.

of the parent acid a fairly smooth relationship emerges. (Logarithmic abscissæ are used to avoid crowding the scale at lower values of k: no theoretical significance is implied). The sequence $T(CO_2) < T(CO) < T(CH\!:\!CH)$ corresponds to onset of C^2, R/C^1, and A^2 scission, respectively, the specific volatile key-product of each being readily detectable

[5] Part XX, Muir and Ritchie, *J.*, 1963, 2692.
[6] Norris and Cresswell, *J. Amer. Chem. Soc.*, 1934, **56**, 423.

(see Experimental section). The position of the minor B^2 scission in the temperature sequence is not known, since keten (the most suitable key-product) could not be detected. $T(\text{Me·CHO})$ is the lowest temperature at which any breakdown is observed: the origin of the acetaldehyde is discussed in the next section.

The results may be compared with those of Smith and Wetzel[7] in a related study of the simple A^1 scission of cyclohexyl esters of substituted benzoic acids. For *meta* and *para*-substitution, they found a linear relation between k and an empirical " characteristic temperature " at which the yield of scission products of each ester passes through a maximum in a series of pyrolyses. (*ortho*-Substitution raises the characteristic temperature, with departure from the linear relation.) Other cognate parameters can be used in place of k: for example, Smith and Wetzel[7] found a direct relation between characteristic temperature and the infrared O–R stretching frequency of the esters. Similarly, recent work[8] (to be published later) on the esters $EtO_2C·[CH_2]_n·CO_2Et$ reveals a novel periodicity when either the O–R stretching frequency of each ester or $T(CH_2:CH_2)$ is plotted against n.

It is not claimed that the onset temperatures for all types of substituents in the aromatic ring will necessarily fall on the smooth curves of the Figure. In fact, preliminary work with the vinyl nitrobenzoates suggests that this may not be so: and the point is being further studied.

Origin of Acetaldehyde: The A^1/D Reaction.—In earlier pyrolyses[2,3] of vinyl benzoate, where residence times in the flow-reactor were much shorter than in the present work (*ca.* 15—20 sec., as against *ca.* 130—220 sec.), no acetaldehyde was detected: but its present formation can readily be interpreted in the light of more recent work.[9,10] Partial polymerisation of the ester is promoted by high residence times; and acid is then stripped from the polymer, presumably by the type of non-radical chain reaction observed[11] for poly(vinyl acetate), leaving a dark polymeric residue believed to be a conjugated polyene. As it is formed, the acid reacts with unchanged monomer, yielding an ethylidene diester, which disproportionates (*D*) to acid anhydride and acetaldehyde, thus:[3]

$$R·CO_2·CH:CH_2 + R·CO_2H \longrightarrow (R·CO_2)_2CHMe \xrightarrow{D} (R·CO)_2O + Me·CHO$$
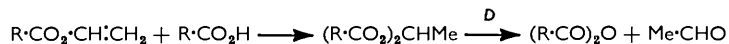
The overall acetaldehyde-producing reaction may be given the notation A^1/D, to indicate its two essential stages (cf. the notation R/C^1).

This concept is readily confirmed. For example, if vinyl *o*-chlorobenzoate is maintained for 20 min. at 250° [*i.e.*, above its $T(\text{Me·CHO})$ but below its $T(CO_2)$: see Figure], acetaldehyde is the only volatile product, and the residue contains *o*-chlorobenzoic acid and anhydride, some unchanged monomer, and the presumed conjugated polyene. The A^1/D reaction has here been completely isolated from competition by reactions C^2, R/C^1, and A^2, all of which have onset temperatures higher than 250°. This absence of A^2 scission clearly shows that free acid must have arisen in some other reaction: and the accompanying scheme shows the best interpretation of the overall breakdown.

This picture agrees well with the views of Goodings[9] and Rashbrook and Taylor,[10] apart from a single discrepancy, not yet explained. The latter workers found that static pyrolysis of vinyl benzoate (*ca.* 450°) leads to complete decomposition, and that the complex pyrolysate includes some 20% of biphenyl; whereas biphenyl was not observed in previous work[2,3] with a flow-reactor (*ca.* 450—550°). Recent critical repetition of this work has shown[12] that biphenyl is in fact produced, but occurs in the pyrolysate to the extent of only a minute trace.

Clearly, $T(\text{Me·CHO})$ for the *overall* A^1/D breakdown cannot be lower than the onset

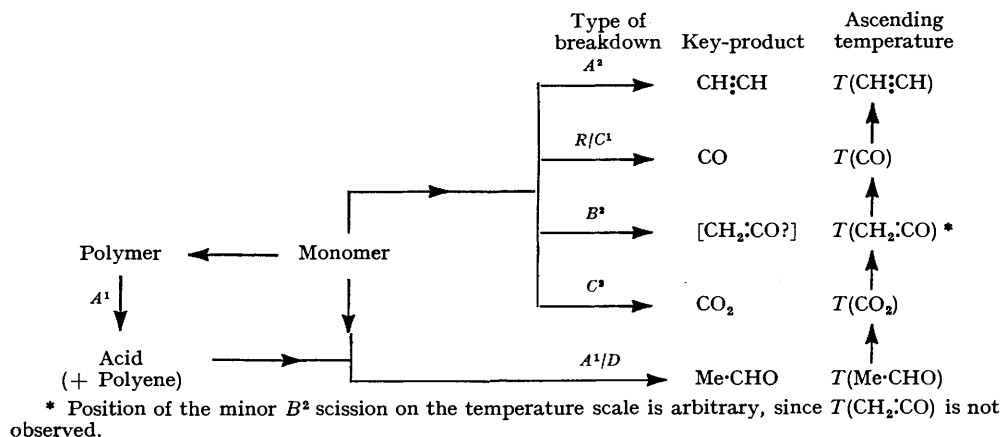[7] Smith and Wetzel, *J. Amer. Chem Soc.*, 1957, **79**, 875.

[8] Reininger, Ph.D. Thesis, Glasgow University, 1961, p. 117.

[9] Goodings, in " Thermal Degradation of Polymers," Soc. Chem. Ind. Monograph No. 13, 1961, p. 211.

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

[11] Grassie, *Trans. Faraday Soc.*, 1952, **48**, 379; 1953, **49**, 835; *Trans. Plastics Inst.*, 1960, **28**, 233.

[12] Ritchie and Yousufzai, unpublished work.

	Type of breakdown	Key-product	Ascending temperature

* Position of the minor B^2 scission on the temperature scale is arbitrary, since $T(CH_2:CO)$ is not observed.

temperature of the controlling step (*i.e.*, A^1 scission of the polymer). Since the addition–disproportionation sequence for vinyl benzoate proceeds smoothly [3] at *ca.* 200° when the ester is refluxed with benzoic acid, the fact that $T(Me \cdot CHO) = 283°$ for vinyl benzoate *alone* (Table 5) must mean that the controlling A^1 scission of polymer occurs at 283°, the liberated acid at once reacting with monomer, with evolution of acetaldehyde. This at first sight suggests a discrepancy between $T(Me \cdot CHO)$, which in the Figure lies within the range *ca.* 235—295° for all the esters, and the higher A^1 scission temperatures observed for simple alkyl esters in general. However, each ester grouping in the polymer chain is secondary, and it is known that branching in the alkyl group of an ester reduces its thermal stability: further, when once a single acid molecule has broken away from the poly(vinyl carboxylate) chain, by whatever mechanism, the next A^1 scission will be rendered easier [11] by the proximity of the activating olefinic group. The temperature discrepancy, then, is more apparent than real.

Previous work [11] suggested that the residual unsaturated polymer, after pyrolytic stripping of acid from a poly(vinyl carboxylate), has predominantly a conjugated polyene structure. The ultraviolet absorptions of the present polymeric residues are consistent with this idea, a series of small bands centred at 540 mμ indicating [13] a conjugated system of some 14 double bonds; but their infrared spectra suggest that in addition some acetylenic and allenic groupings are present. There is marked absorption in the region 2000—2250
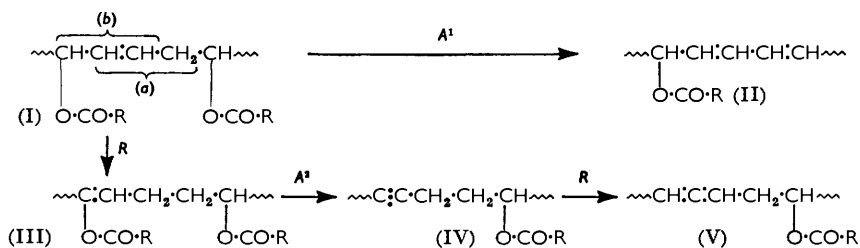
(C:C) and at 3300 (C–H stretching in CH:CR), 2240 (CR:CR'), 1960 cm.$^{-1}$ (C:C:C).[14] The following explanation is tentatively advanced. The first random A^1 scission creates a structure (I) containing two overlapping allylic systems (*a*) and (*b*); and the new double bond activates principally the CH_2 group in (*a*),[11] so that the next elimination favours

[13] Karrer and Jucker, "Carotenoids," Elsevier, New York, 1950, p. 159.
[14] Cross, "An Introduction to Practical Infra-Red Spectroscopy," Butterworths Scientific Publns., London, 1960, p. 58.
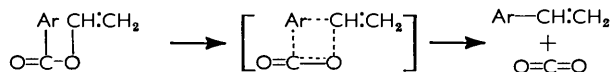
formation of the conjugated structure (II), probably by the conventional cyclic transition-state [15] for A^1 scission. However, another less strongly activated elimination of acid may compete with the foregoing. It is shown later that allyl benzoate, a model for system (*b*), undergoes, *inter alia*, a minor scission to acid and propyne (probably a direct A^2 scission after partial rearrangement of the allyl ester to its propenyl isomer). Hence, the polymer may break down mainly to the conjugated system (II), but may also in part rearrange to (III) and then by A^2 scission afford the acetylenic system (IV); further, this system is capable [16] of thermal rearrangement to the allenic system (V). Finally, if the original thermal polymerisation terminates by disproportionation, half of the chains will have terminal unsaturation and would react as follows on pyrolysis:

$$\text{∿CH}_2\text{·CH·CH:CH·O·CO·R} \xrightarrow{\;A^1\;} \text{∿CH:CH·CH:CH·O·CO·R} \xrightarrow{\;A^2\;} \text{∿CH:CH·C:CH}$$
$$\quad\;\; | \qquad\qquad\qquad\qquad$$
$$\quad\; \text{O·CO·R}$$

There is precedent for all these reactions, which between them explain all the above-mentioned infrared absorptions.

Discussion of Primary Scissions.—Decarboxylation (C^2). Each chloro-ester yields a chlorostyrene retaining essentially the orientation of the parent ester; but critical examination by gas–liquid chromatography and infrared spectrometry, with the help of pure reference compounds, shows that the *m*-chlorostyrene contains a minor amount of its *o*- and a trace of its *p*-isomer, and the *p*-chlorostyrene a trace of its *o*-isomer. Only the *o*-chlorostyrene shows no measurable change of orientation.

This suggests that in C^2 scission two mechanisms operate, the major one preserving the orientation and the minor one leading to a change. This may well be connected with the observation [17] that vapour-phase decarboxylation (*ca.* 520°) is mainly a homogeneous reaction, but also, in part, occurs heterogeneously at the reactor wall. Neither reaction, it appears, is free-radical in nature, since decarboxylation could not be affected by inhibitor techniques.[17] The most likely interpretation is that the major mechanism is intramolecular, involving some such cyclic transition state as that annexed, in which the aryl grouping is at no stage wholly detached from an adjacent carbon atom, so that there is no opportunity for change of orientation.

$$\begin{array}{c} \text{Ar}\;\;\text{CH:CH}_2 \\ |\quad\; | \\ \text{O=C-O} \end{array} \longrightarrow \left[\begin{array}{c} \text{Ar}\cdots\text{CH:CH}_2 \\ | \qquad\;\; \\ \text{O=C}\cdots\text{O} \end{array}\right] \longrightarrow \begin{array}{c} \text{Ar—CH:CH}_2 \\ + \\ \text{O=C=O} \end{array}$$

It is of interest that there is also evidence [18] for duality of mechanism in the analogous C^2 scission of esters such as $\text{R·CH:CH·CO}_2\text{Ar}$.

Acyl–oxygen scission (B^2). Each chloro-ester yielded a small amount (Table 2) of the corresponding chlorobenzaldehyde, with no detectable change of orientation: also, benzaldehyde is formed in traces from vinyl benzoate.[5] In no case, however, was keten detected, and it is therefore uncertain whether the aromatic aldehyde is formed by B^2 scission or by an unknown side-reaction.

Mere failure to detect a trace of keten does not exclude B^2 scission, since keten, run into the reactor (*ca.* 500°) in benzene solution, is largely destroyed under these conditions (over 75%; cf. Young [19]). It is considered, therefore, that a very minor B^2 scission competes in the pyrolysis of vinyl chlorobenzoates and benzoate:

$$\text{Ar·CO} \;\vdots\; \text{O·CH:CH}_2 \longrightarrow \text{Ar·CHO} + \text{CH}_2\text{:CO} \qquad . \;\; . \;\; . \;\; . \;\; . \;\; . \quad B^2$$
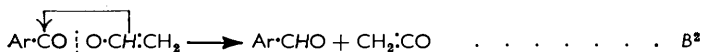
[15] Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.
[16] Meinert and Hurd, *J. Amer. Chem. Soc.*, 1930, **52**, 4549; Hurd and Meinert, *ibid.*, 1931, **53**, 292; Hurd and Christ, *ibid.*, 1937, **59**, 2161.
[17] Part XXI, Bengough, Ritchie, and Steedman, *J.*, 1963, 2697.
[18] Part XIX, Reininger, Ritchie, and Ferguson, succeeding paper.
[19] Young, *J.*, 1958, 2909.

Rearrangement–decarbonylation (R/C^1). The halogen atom hardly affects the yield of aryl methyl ketone (Table 2); also, the latter shows no evidence for change of orientation during the rearrangement R. This is consistent with our mechanism [2] for the R/C^1 reaction, based on a four-centre transition-state (as proposed by Young et al.[20]) in which the aryl group is at no stage completely detached from the adjacent carbon atom.

The small amounts of chlorotoluene and toluene (Table 2) are attributed to minor secondary decarbonylation of the methyl ketone formed by R/C^1 reaction: the amounts formed were so small that no evidence could be obtained for or against change of orientation in this secondary reaction.

Alkenyl–oxygen scission (A^2). It is suggested that this occurs by the same type of cyclic transition-state as proposed [15] for alkyl-oxygen (A^1) scission. Models show that for
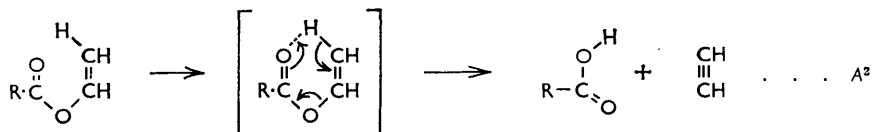
both alkyl and alkenyl esters the β-hydrogen and the carbonyl-oxygen atom can approach each other sufficiently closely: but the slight strain produced by the C:C group is reflected by the higher onset temperature for A^2 scission.

In the Figure, $T(\text{CH:CH})$ for A^2 scission and $T(\text{Me·CHO})$ for A^1 scission (of polymer) are similarly and markedly k-dependent, whereas $T(\text{CO})$ and $T(\text{CO}_2)$ form another pair, similarly but this time less markedly k-dependent. A parallel division into two reaction categories is shown by a recent observation [21] (to be published later) that the presence of certain metallic catalysts markedly depresses $T(\text{CH:CH})$ and $T(\text{Me·CHO})$ but does not affect $T(\text{CO})$ or $T(\text{CO}_2)$. This is consistent with the view that A^2 scission has the same type of mechanism as A^1 scission, which was at one time widely regarded as molecular but, in the view of Maccoll,[22] is quasi-heterolytic though unimolecular.

The amount of acid liberated in A^2 scission is markedly greater than a molar equivalent of the acetylene liberated (Table 3). The excess of acid has previously been accounted for: and the true index of the extent of A^2 scission is the yield of alkyne, not of acid.

TABLE 3.

Molar yield of acid and alkyne from $\text{X·C}_6\text{H}_4\text{·CO}_2\text{·CH:CH}_2$ (based on monomer destroyed during pyrolysis).

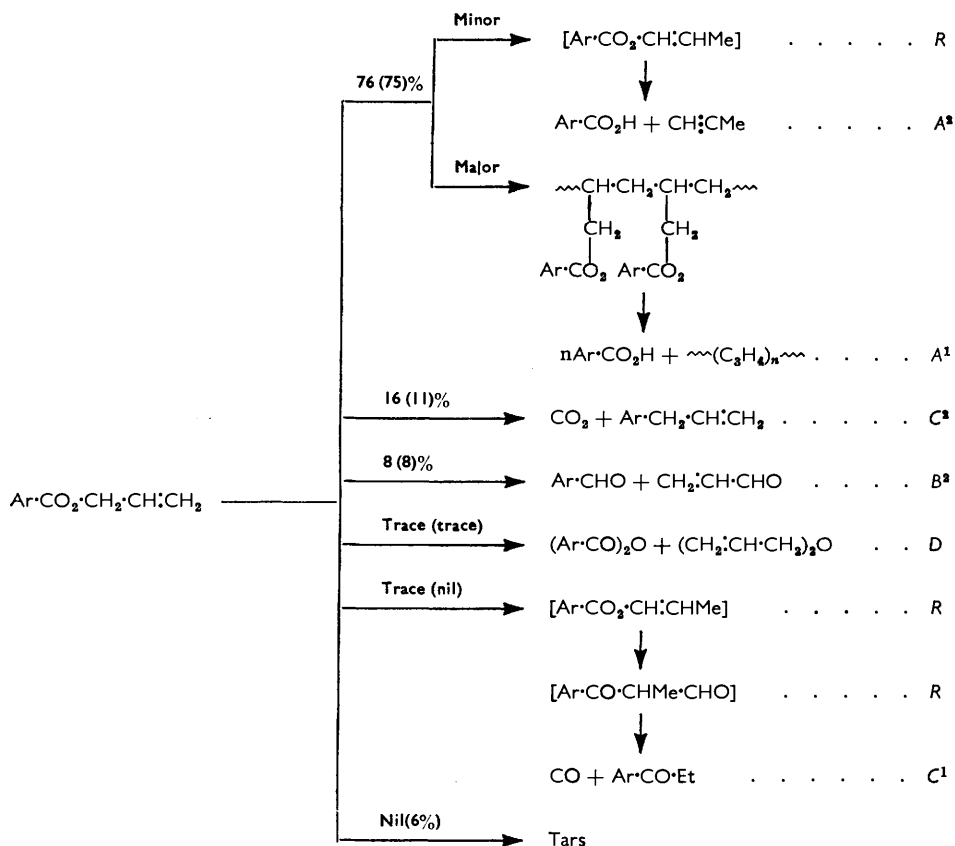| Product	X = o-Cl	m-Cl	p-Cl	H
$\text{X·C}_6\text{H}_4\text{·CO}_2\text{H}$	0·17	0·19	0·25	0·11
Acetylene	0·05	0·10	0·07	0·03

Allyl Benzoate and o-Chlorobenzoate.—Overall breakdown. At ca. 500°, this is much more complex than indicated by earlier work [3] on allyl benzoate. The results are best interpreted by the annexed reaction scheme. The reactions are there arranged in approximate order of abundance, rather than of onset temperatures, which have not been measured because of the complexity of the system. The figures show the approximate contributions from the benzoate and (in parentheses) the o-chlorobenzoate. In addition, each ester yields the following minor products: ArH and water (from C^2 scission and dehydration,[4] respectively, of free acid), ethylene (probably mainly from C^1 scission of acraldehyde [23]), and a little ArMe, methane, and hex-1-ene (origin uncertain).

[20] Young, Frostick, Sanderson, and Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 3635.
[21] Ramsay, M.Sc. Thesis, Glasgow University, 1963, Part II.
[22] Maccoll, *J.*, 1958, 3398.
[23] Mackinnon, Ph.D. Thesis, Glasgow University, 1959, p. 34.

Minor

76 (75)% → [Ar·CO$_2$·CH:CHMe] . . . . . R

↓

Ar·CO$_2$H + CH:CMe . . . . . A^2

Major

$\sim\sim$CH·CH$_2$·CH·CH$_2\sim\sim$

| |
CH$_2$ CH$_2$
| |
Ar·CO$_2$ Ar·CO$_2$

↓

nAr·CO$_2$H + $\sim\sim$(C$_3$H$_4$)$_n\sim\sim$ . . . . . A^1

16 (11)% → CO$_2$ + Ar·CH$_2$·CH:CH$_2$ . . . . . C^2

8 (8)% → Ar·CHO + CH$_2$:CH·CHO . . . . B^2

Ar·CO$_2$·CH$_2$·CH:CH$_2$ ——

Trace (trace) → (Ar·CO)$_2$O + (CH$_2$:CH·CH$_2$)$_2$O . . D

Trace (nil) → [Ar·CO$_2$·CH:CHMe] . . . . . R

↓

[Ar·CO·CHMe·CHO] . . . . . R

↓

CO + Ar·CO·Et . . . . . . C^1

Nil(6%) → Tars

Nature of Competing Reactions.—The predominating reaction is formation of free acid, apparently by two different reactions. The esters yield a little propyne: and this is conceivably due to an A^1 scission to acid and allene, with rearrangement. However, an alk-1-yne in general rearranges thermally to an alka-1,2-diene, whereas the reverse change requires a catalyst: [16] hence, it is more likely that a little of the allyl ester first rearranges to its propenyl isomer and this by direct A^2 scission affords acid and alkyne. (The same preliminary rearrangement is thought to be responsible for the trace of propiophenone formed by the benzoate; with the double bond transferred from the βγ- to the αβ-position, the ester can undergo the same kind of R/C^1 scission as a vinyl ester.) However, the acid formed is very much more than a molar equivalent of the alkyne and must have another major source; and it is found that allyl esters, like their vinyl analogues, partially polymerise during pyrolysis, with subsequent A^1 elimination of acid and formation of an unsaturated polymer. Direct multiple A^1 scission would lead to a non-conjugated polymer, which would perhaps rearrange thermally to a conjugated form, thus:

$\sim\sim$CH$_2$·C·CH$_2$·C·CH$_2$·C$\sim\sim$? $\sim\sim$CH:C·CH:C·CH:C$\sim\sim$
    ‖   ‖   ‖   → | | |
   CH$_2$ CH$_2$ CH$_2$ Me   Me   Me
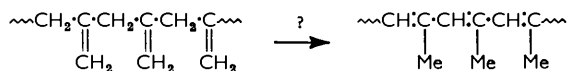
Unlike vinyl benzoate, allyl benzoate yields no acetaldehyde on pyrolysis. This is because an allyl ester reacts with free acid on being heated,[24] to yield only a 1,2-diester, which (unlike the 1,1-diester formed by vinyl esters) cannot undergo disproportionation with formation of acetaldehyde.

[24] von Béhal and Desgrez, *Compt. rend.*, 1892, **114**, 676.

The B^2 and C^2 reactions of allyl benzoate are already known,[3] and it need only be noted (i) that B^2 scission is much more pronounced than its rather doubtful trace-equivalent for vinyl benzoate, and (ii) that C^2 scission of allyl *o*-chlorobenzoate yields *o*-allylchlorobenzene, with no evidence for a change in orientation (as in C^2 scission of vinyl *o*-chlorobenzoate).

The very minor disproportionation (D) of allyl benzoate to acid anhydride and an ether has a parallel in the pyrolysis of benzyl benzoate and some of its derivatives: [25] but a little of the observed anhydride is probably due to direct dehydration of free acid,[4] since a trace of water is observed in the pyrolysate.

EXPERIMENTAL

General Methods.—Pyrex-glass flow-reactors were used, as in previous work: [2,3] they were cleaned by heating them in a current of air (*ca.* 500°), and thoroughly flushed with nitrogen, before each run, to ensure substantially (but not rigorously) oxygen-free conditions. Residence times were calculated as previously.[3]

Aldehydes were characterised as their 2,4-dinitrophenylhydrazones, by means of paper chromatography.[26] Other solid pyrolysate components or their derivatives were identified by mixed m. p.s. Acid anhydrides were detected by the Davidson–Newman colour reaction,[4] and free water by the anhydrous copper sulphate test. For many runs, products were identified by gas–liquid chromatography and/or infrared spectrometry. Previous calibration of the chromatography unit permitted quantitative analysis which, although not of a high order of accuracy because of the complex mixtures examined, gave valuable results. Where a component is reported as identified by gas–liquid chromatography, the retention time agreed to within ± 0.1 min. (usually with precise correspondence) with that of a pure reference sample under identical conditions. The instruments used were a Griffin and George mark II B and a Pye argon: the columns were packed with (i) 20% Silicone E 301 on Celite 545 or (ii) 20% Apiezon N on Celite 545. In doubtful cases the identification was confirmed by infrared spectrometry (*e.g.*, for *m*- and *p*-chlorostyrene, which are not resolved chromatographically).

Measurement of Onset (Threshold) Temperatures.—The apparatus was a slight modification of one devised by Mackinnon.[27] The pyrolysand (*ca.* 1 g.) is placed in a Pyrex test tube (diam. 1 in., height 5·5 in.), with a thermocouple pocket 1·5 in. from the bottom, and a ground-in stopper with a tube at the top for exit gases and a central lead-in tube, reaching to within 2 in. of the bottom, for passage of a stream of inert carrier nitrogen. This reactor is enclosed in a vertical electric furnace, and the temperature (recorded continuously) is raised at a standard rate of 1°/min. The nitrogen stream (flow-rate *ca.* 0·1 l./min.) carries any volatile breakdown products, through the exit tube, into a water-cooled condenser (to return unchanged pyrolysand continuously to the reactor) and into an optical cell located between a constant-voltage light-source and a photocell connected to a Pye amplifier-galvanometer. The optical cell contains a simple reagent giving a colour change or turbidity specific for the volatile key-product sought in each run. The reagents used were: For alkenes, bromine in carbon tetrachloride (dilute). For alkynes, silver nitrate in ethanol–water (dilute). For aldehydes and ketones, 2,4-dinitrophenylhydrazine in hydrochloric acid (saturated). For carbon monoxide, phosphomolybdic acid and palladium chloride in hydrochloric acid (dilute). For carbon dioxide, aqueous calcium hydroxide (saturated); alternatively, aqueous sodium hydrogen carbonate and Methyl Red, adjusted to the colour-change point.

As soon as the onset temperature is reached, a trace of key-product in the carrier gas causes a sharply defined decrease in the recorded steady output of the photocell. Onset temperatures are measurable with an error of *ca.* $\pm 3°$; runs are normally in duplicate, and the very occasional erratic result is dealt with by several additional runs.

The apparatus is effective only for pyrolysands boiling above *ca.* 150°: if more highly volatile, they tend to be swept into the optical cell along with the key-products and may interfere seriously with the colour change.

Preparation of Pyrolysands.—*Purity.* All materials were checked by gas–liquid chromatography for purity before pyrolysis.

[25] Jones and Ritchie, *J.*, 1960, 4141.
[26] Burton, *Chem. and Ind.*, 1954, 576.
[27] Mackinnon, ref. 23, p. 89.

Vinyl o-, m-, and p-chlorobenzoate. The esters were prepared by Ham and Ringwald's ester-interchange method,[28] the purity of the redistilled and/or recrystallised products being confirmed by gas–liquid chromatography. The o-chlorobenzoate (28%) had b. p. 113°/11 mm. (lit.,[29] b. p. 116—118°/14 mm.); the m-isomer (26%), b. p. 104°/8 mm. (lit.,[29] b. p. 84—86°/ 0·025 mm.); the p-isomer (26%), b. p. 106—110°/9 mm., m. p. 49° (lit.,[29] b. p. 118—120°/14 mm., m. p. 49—50°).

Vinyl benzoate. A pure specimen prepared by Dr. W. M. Muir[5] was used.

Allyl benzoate. Prepared (68%) by Perkin's method,[30] the ester had b. p. 88—90°/5 mm. (lit.,[3] b. p. 78—80°/2 mm.).

Allyl o-chlorobenzoate. Prepared (64%) by the same method, this *ester* had b. p. 125°/9 mm. (Found: C, 61·7; H, 4·9; Cl, 17·4. $C_{10}H_9ClO_2$ requires C, 61·2; H, 4·7; Cl, 17·8%).

Keten. This was used as a solution in benzene. Keten was prepared by pyrolysis of acetic anhydride (*ca.* 500°): it was condensed in a liquid-nitrogen trap and purified by distillation into a cold trap containing solidified benzene, in which it dissolved at room temperature.

Reference standards. The following were obtained from commercial sources: o- and p-chloro-acetophenone; o-, m-, and p-chlorostyrene: o-, m-, and p-chlorobenzaldehyde; o-, m-, and p-chlorobenzoic acid. m-Chloroacetophenone was prepared by standard methods.

Results.—The general conditions for 9 pyrolyses are summarised in Table 4: detailed results are given below. Onset temperatures are given in Table 5.

TABLE 4.

Pyrolysis (*ca.* 500°) of vinyl o-, m-, and p-chlorobenzoate and vinyl benzoate, and of allyl benzoate and o-chlorobenzoate.

		Vinyl o-chloro-benzoate		Vinyl m-chloro-benzoate		Vinyl p-chloro-benzoate		Vinyl benzoate	Allyl benzoate	Allyl o-chloro-benzoate
Run:		1	2	3	4	5	6	7	8	9
Feed-rate (g. min.)		0·35	0·33	0·29	0·30	0·35	0·31	0·28	0·21	0·25
Residence time (sec.) ...		150	140	160	155	135	150	135	195	200
Wt. pyrolysed (g.)		30·0	30·0	30·0	30·0	30·0	30·0	30·0	20·0	20·0
Pyrolysate:										
(*a*) In main receiver (g.)		21·0	20·0	19·5	21·0	20·0	21·0	24·0	15·0	15·0
(*b*) In cold trap (g.) ...		—	Trace	—	Trace	Trace	—	—	1·0	2·0
(*c*) Gaseous (l.)		4·2	4·3	4·2	4·2	4·4	4·0	3·3	3·0	2·4
Unchanged pyrolysand(g.)		3·5	3·7	3·0	—	3·0	—	7·3	10·0	5·6
Composition (%) of gas (*c*) (approx.):										
CO		76	76	80·5	81·5	79·5	79·5	80	26·5	20·5
CO_2		17	18	9	9	13	13	14	52·5	58
Alkenes		3	3	2·5	2·5	2	2	3	*	*
Alkynes		4	3	8	7	5·5	5·5	13	*	*
Sat. hydrocarbons		Trace	Trace	Trace	Trace	Trace	Trace	Trace	2	Trace

* Not determined separately: total unsaturated hydrocarbons 19% (run 8), 21·5% (run 9).
— Not observed.

TABLE 5.

Onset temperatures of reactions competing in the pyrolysis of $X·C_6H_4·CO_2·CH\!:\!CH_2$.

(Each figure is the mean of several concordant results by at least two observers.)

X	$T(Me·CHO)$	$T(CO_2)$	$T(CO)$	$T(CH\!:\!CH)$
o-Cl	235°	290°	322°	340°
m-Cl	255	295	332	384
p-Cl	272	298	336	390
H	283	303	342	415
p-Me	295	304	353	423

Pyrolysis of Vinyl o-Chlorobenzoate.—*Runs 1 and 2.* Runs 1 and 2 gave closely similar results: those of Run 2 are given here. The aldehyde trap yielded only the derivative of acet-aldehyde (paper chromatography[26]): the aniline–ether trap gave no evidence for keten. The gaseous pyrolysate (*c*) contained acetylene, ethylene, and methane: a trace of water was

[28] Ham and Ringwald, *J. Polymer Sci.*, 1952, **8**, 91.
[29] Hopff and Lüssi, *Makromol. Chem.*, 1956, **18/19**, 227.
[30] Perkin, *J.*, 1896, **69**, 1226.

identified in the cold trap. Liquid (*a*) contained suspended *o*-chlorobenzoic acid (1·0 g.): the filtrate, when distilled, yielded (i) 6·0 g., b. p. 24—64°/5 mm., (ii) 6·0 g., b. p. 64—84°/5 mm., (iii) 4·0 g., b. p. 84—104°/4 mm., (iv) 0·3 g., b. p. 110°/4 mm., and (v) 3 g. of higher-boiling residue. Fraction (i), redistilled, yielded (*ia*) 0·4 g. of chlorobenzene (infrared) and (*ib*) 5·6 g., which contained (gas–liquid chromatography) chlorobenzene, *o*-chlorotoluene, *o*-chlorostyrene, *o*-chlorobenzaldehyde, *o*-chloroacetophenone (confirmed as 2,4-dinitrophenylhydrazone), unchanged pyrolysand, and a trace of unidentified material. Fractions (ii) and (iii) contained *o*-chloroacetophenone and unchanged pyrolysand, fraction (iii) being mainly the latter. Fraction (iv) and residue (v) consisted of *o*-chlorobenzoic acid, the residue also giving the colour reaction [4] of an acid anhydride. Infrared spectrometric examination of fraction (*ib*) confirmed the presence of *o*-chlorostyrene and the absence of its *m*- and *p*-isomers.

Pyrolysis of Vinyl m-*Chlorobenzoate.*—*Runs 3 and 4.* These runs gave closely similar results: those of Run 4 are given here. The aldehyde trap showed only acetaldehyde: gas (*c*) contained acetylene, ethylene, and methane (infrared): water was identified in the cold trap. Liquid (*a*), distilled, yielded (i) 1·5 g., b. p. 22—66°/4 mm., (ii) 12·0 g., b. p. 66—80°/4 mm., (iii) 2·5 g., b. p. 50—86°/4 mm., and (iv) 4·8 g. of higher-boiling residue. Fraction (i) contained (gas–liquid chromatography) chlorobenzene, *m*-chlorotoluene, *m*-chlorostyrene, *m*-chlorobenzaldehyde, *m*-chloroacetophenone, unchanged pyrolysand, and a trace of unidentified material. Fraction (ii) contained chlorobenzene, *o*- and *m*-chlorostyrene, *m*-chlorobenzaldehyde, *m*-chloroacetophenone (confirmed as semicarbazone), and unchanged pyrolysand: fraction (iii) contained the two last-named substances. Residue (iv) was *m*-chlorobenzoic acid, together with an acid anhydride. Fraction (ii) yielded only a single 2,4-dinitrophenylhydrazone (paper chromatography [26]), that of *m*-chloroacetophenone. The *m*- and *p*-isomer of chlorostyrene are not resolved by gas–liquid chromatography: but infrared spectrometric examination of fraction (ii) showed that a trace of the *p*-isomer (faint bands at 833, 1018, and 1090 cm.⁻¹) was present in the *m*-isomer. It also confirmed the presence of a little *o*-isomer (bands at 770, 1132, 1042, and 1095 cm.⁻¹).

Pyrolysis of Vinyl p-*Chlorobenzoate.*—*Runs 5 and 6.* These runs gave closely similar results: those of Run 5 are given here. The aldehyde trap showed only acetaldehyde: water was identified in the cold trap. Liquid (*a*), distilled, yielded (i) (5 g., b. p. 25—50°/12 mm., (ii) 10·0 g., b. p. 50—110°/12 mm., (iii) 4·0 g., b. p. 110—140°/12 mm., and (iv) 2·8 g. of higher-boiling residue. Fraction (i) contained (gas–liquid chromatography) chlorobenzene, *p*-chlorotoluene, *p*-chlorostyrene, *p*-chlorobenzaldehyde, *p*-chloroacetophenone, unchanged pyrolysand, and a trace of unidentified material: fraction (ii) was mainly *p*-chloroacetophenone (the total 2,4-dinitrophenylhydrazone showed the presence of only a single carbonyl compound; paper chromatography [26]); fraction (iii) contained *p*-chloroacetophenone and unchanged pyrolysand; residue (iv) was *p*-chlorobenzoic acid together with an acid anhydride. Although chromatography revealed *p*-chlorostyrene in fraction (i), infrared spectrometry also showed very weak bands at 1042 and 1132 cm.⁻¹ (aromatic *ortho*-substitution) which were present in a reference spectrum of pure *o*-chlorostyrene.

Pyrolysis of Vinyl Benzoate.—*Run 7.* The aldehyde trap showed only acetaldehyde. The total non-gaseous pyrolysate (*a*) contained (gas–liquid chromatography) benzene, toluene, styrene, acetophenone, unchanged pyrolysand, benzoic acid, a trace of unidentified material, and a trace of a further product with a retention time very close to that of pure benzaldehyde as a reference sample. Pyrolysate (*a*) also contained an anhydride. Keten could not be identified in gas (*c*).

Pyrolysis of Allyl Benzoate.—*Run 8.* Liquid (*a*) contained 3 g. of suspended benzoic acid: the filtrate, distilled, yielded (i) 0·5 g., b. p. 20—60°/4 mm., (ii) 6·3 g., b. p. 60—90°/4 mm., (iii) 4·4 g., b. p. 90—115°/4 mm., and (iv) 0·8 g. of higher-boiling residue. Fraction (i) contained (gas–liquid chromatography) diallyl ether, benzene, toluene, and allylbenzene: fraction (ii) contained allylbenzene, benzaldehyde, propiophenone (trace), unchanged pyrolysand, and *ca* 0·5% of two unidentified products: fraction (iii) contained benzaldehyde, unchanged pyrolysand, and benzoic acid. Residue (iv) contained benzoic acid and tar. Gas (*c*) contained (infrared) hex-1-ene (bands at 738, 914, 998, 1456, 1647, 1820, 2960, and 3080 cm.⁻¹), propyne (1244, 1269, 1440, 1460, 2160, and 3380 cm.⁻¹), and methane (1300 cm.⁻¹). The liquid (*b*) in the cold trap contained hex-1-ene, propyne, ethylene, methane, acraldehyde, and water (the two latter remaining in the trap after the other four had been allowed to volatilise at room temperature).

Pyrolysis of Allyl o-Chlorobenzoate.—*Run* 9. Liquid (*a*), distilled, yielded (i) 2 g., b. p. 20—40°/17 mm., (ii) 1 g., b. p. 80—130°/17 mm., (iii) 5·5 g., b. p. 130—150°/10 mm., and (iv) 6·5 g. of higher-boiling residue. Fraction (i) contained (gas–liquid chromatography) chloro-benzene, with traces of diallyl ether and *o*-allylchlorobenzene: fraction (ii) contained chloro-benzene, *o*-chlorotoluene, *o*-allylchlorobenzene, *o*-chlorobenzaldehyde, unchanged allyl *o*-chloro-benzoate, and an unidentified component. Fraction (iii) contained suspended *o*-chlorobenzoic acid (2·5 g.); the filtrate was mainly unchanged pyrolysand, but was reddish. The infrared spectrum of gas (*c*) was almost identical with that of gas (*c*) from allyl benzoate (Run 8): similarly, liquid (*b*) from the cold trap left a residue of acraldehyde (0·2 g.) after evaporation of the volatile gases.

Infrared Spectra.—The infrared absorption spectra of the following compounds have been recorded: vinyl *o*-chlorobenzoate (D.M.S. Index No. 9918): vinyl *m*-chlorobenzoate (D.M.S. Index No. 9927): vinyl *p*-chlorobenzoate (D.M.S. Index No. 9919): allyl *o*-chlorobenzoate (D.M.S. Index No. 9920).