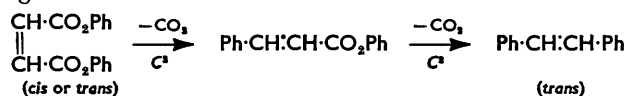


498. *Studies in Pyrolysis. Part XI.\* Competitive Routes in the Pyrolysis of Esters: Phenyl Acrylate and Phenyl  $\alpha$ -Methylacrylate.*

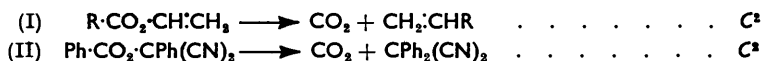
By H. M. MACKINNON and P. D. RITCHIE.

Pyrolysis of phenyl acrylate (or  $\alpha$ -methylacrylate) in the vapour phase occurs at *ca.* 550° mainly by two competitive routes: (i) intra-acyl scission to acetylene (or methylacetylene) and phenyl formate, with secondary decarbonylation of the latter to phenol and carbon monoxide, and (ii) decarboxylation to styrene (or  $\alpha$ -methylstyrene) and carbon dioxide. Reaction (i), which predominates, is suppressed by the addition of quinol to the pyrolysand; reaction (ii) is not. A tentative free-radical mechanism for reaction (i) is suggested. Minor competitive primary and secondary reactions are described.

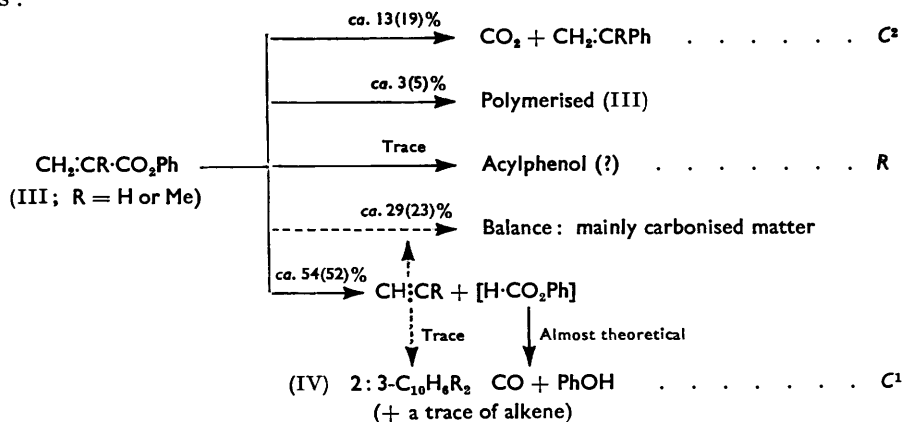
ALTHOUGH thermal decarboxylation of many carboxylic acids is well established,<sup>1</sup> decarboxylation of their esters was for long represented by only very few examples,<sup>2,3</sup> such as the following: <sup>2</sup>



Recently, however, decarboxylation ( $\text{C}^2$ ) has been observed<sup>4</sup> as a competitive route in the complex pyrolysis of various vinyl carboxylates (I), and also<sup>5</sup> of  $\alpha\alpha$ -dicyanobenzyl benzoate (II):



It now seems probable, therefore, that the  $\text{C}^2$  reaction is more important in ester pyrolysis than previously appeared, and deserves further study. A comparison of the pyrolysis<sup>4</sup> of vinyl benzoate (I; R = Ph) with that of its structural isomer, phenyl acrylate, suggested itself as a first step in studying the factors which dictate that an ester shall undergo thermal decarboxylation. It has now been found that phenyl acrylate (III; R = H) and phenyl  $\alpha$ -methylacrylate (III; R = Me), both of which are remarkably stable up to *ca.* 500°, break down at *ca.* 550° to the extent of *ca.* 50% in the flow system employed (Table I, runs 1—4) by a series of competitive reactions (including decarboxylation), best represented as follows:



\* Part X, preceding paper.

<sup>1</sup> Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chap. 13.

<sup>2</sup> Anschütz, *Ber.*, 1885, 18, 1945; Anschütz and Wirtz, *Ber.*, 1885, 18, 1947; Bischoff and von Hedenström, *Ber.*, 1902, 35, 4084; Anschütz, *Ber.*, 1927, 60, 1320.

<sup>3</sup> Roberts and Bowden, *Rec. Trav. chim.*, 1930, 49, 665.

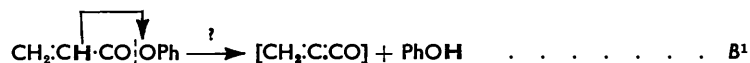
<sup>4</sup> Allan, Forman, and Ritchie, *J.*, 1955, 2717.

<sup>5</sup> Bennett, Jones, and Ritchie, *J.*, 1956, 2628.

The figures above each horizontal arrow represent the approximate weight-contribution of each competing route to the overall pyrolysate from the acrylate and (in parentheses) the  $\alpha$ -methylacrylate; within reasonable limits of experimental error, the molar ratio of the various routes is the same for each pyrolysate. The broken arrows indicate the most probable source of the observed tar, and of the naphthalenes (IV; R = H or Me).

## DISCUSSION

*Intra-acyl Scission.*—The major primary breakdown route shown above, leading to an alkyne and phenyl formate, is of a novel type corresponding to scission within the  $\text{CH}_2\text{:CR}\cdot\text{CO}\cdot$  grouping, which may thus be appropriately designated *intra-acyl scission*. This observation confirms Skraup and Nieten's report<sup>6</sup> that phenyl acrylate breaks down to phenol (64%), carbon monoxide, and acetylene at *ca.* 300–320° (sealed tube; 64 hr.), though these workers did not record decarboxylation or any other competing reaction. Since phenyl acetate (which like the acrylate and  $\alpha$ -methylacrylate is very thermostable) breaks down<sup>7</sup> at *ca.* 600° to keten and phenol by acyl-oxygen ( $B^1$ ) scission, it might be expected that phenyl acrylate would also break down primarily in a similar way, thus:



Although the keten (methyleneketen) predicted on this basis does not appear to be known, it should be highly unstable, and might be expected to break down by a secondary decarbonylation ( $C^1$ ), thus accounting for the other two products accompanying phenol in the pyrolysate:



While the above sequence might formally occur for the acrylate (III; R = H), it is precluded for the  $\alpha$ -methylacrylate (III; R = Me) by replacement of the  $\alpha$ -hydrogen atom **H** by the less mobile methyl group, and cannot explain the formation of phenol (with no evidence for any formation of anisole) on pyrolysis of the latter ester (Table I, runs 3–4). The evidence, therefore, favours the alternative explanation of a primary competitive scission to an alkyne ( $\text{CH:CR}$ ) and phenyl formate. The latter ester is known<sup>8</sup> to break down to carbon monoxide and phenol on distillation; and it is now found (Table I, run 5) that this decarbonylation is almost theoretical in the vapour phase at *ca.* 550°. There is no evidence for formation of benzene by competitive decarboxylation (in marked contrast to the thermal breakdown<sup>3</sup> of triphenylmethyl formate by the  $C^2$ , but not the  $C^1$ , reaction), and not more than a trace of phenyl formate survives in the pyrolysate.

Both acrylate and  $\alpha$ -methylacrylate yield a small trace of phenyl formate, thus confirming the above mode of intra-acyl scission; but the accompanying alkyne ( $\text{CH:CR}$ ) is much less than equivalent in amount to the observed carbon monoxide and phenol (Table I, runs 1–4). This deficiency can be attributed to partial secondary destruction of the alkyne; for example, the observed traces of a naphthalene (IV; R = H or Me) are most probably due to pyrolysis of the alkyne, on the classical lines recorded by Berthelot,<sup>9</sup> though this is of secondary importance to the formation of much carbonised matter and tar. (It has similarly been noted<sup>10</sup> that pyrolysis of phenyl vinyl ether at *ca.* 500°, which yields acetylene and phenol in a molar ratio much less than unity, also leads to heavy carbonisation.) In the present pyrolyses, tar formation from phenyl acrylate can be

<sup>6</sup> Skraup and Nieten, *Ber.*, 1924, 57, 1294.

<sup>7</sup> Ritchie, unpublished observation, 1934.; Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, 60, 2419.

<sup>8</sup> Adickes, Brunnert, and Lückner, *J. prakt. Chem.*, 1931, 130, 163.

<sup>9</sup> Berthelot, *Ann. Chim. Phys.*, 1866, [4], 9, 445.

<sup>10</sup> Iengar and Ritchie, preceding paper.

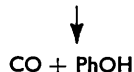
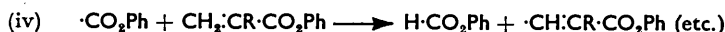
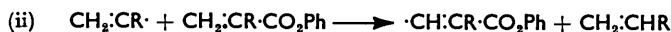
correlated roughly with the extent of intra-acyl scission (cf. Table 2); nevertheless, there must be some tar-producing reaction other than mere secondary breakdown of the alkyne, since there is more carbonised matter than can be accounted for on this basis. This is indicated in the foregoing overall reaction-scheme for the esters (III).

The effect of various inhibitors on the competitive pyrolyses has been studied for the acrylate (III; R = H); and it is found that although the C<sup>2</sup> reaction is not consistently and significantly affected, the intra-acyl scission is completely suppressed by addition of 1% of quinol to the pyrolysand (Table 2). This suggests that the latter breakdown is free-radical in character; and the following sequence is tentatively suggested :

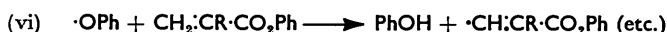
*Initiation*



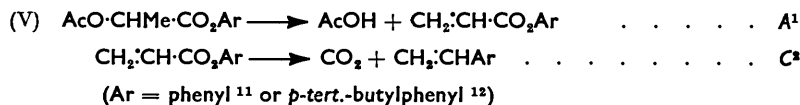
*Propagation*



It is possible that the following stages, (v) and (vi), may compete with (ii), (iii), and (iv); but they cannot represent the only breakdown of the phenoxycarbonyl radicals  $\cdot\text{CO}_2\text{Ph}$ , since they offer no explanation for the observed formation of phenyl formate :



*Decarboxylation (C<sup>2</sup>).*—The present results clarify and reconcile certain apparently conflicting earlier reports. Filachione *et al.*<sup>11, 12</sup> showed that various aryl  $\alpha$ -acetoxypropionates (V), which on pyrolysis yield mainly the predictable A<sup>1</sup> scission products (acetic acid and aryl acrylate), also yield a small amount of a styrene; this result can now be convincingly interpreted by the following reaction sequence :



In addition, however, it was noted<sup>12</sup> that where Ar = *m*-tolyl the pyrolysate (again consisting mainly of the A<sup>1</sup> products) contains a little *m*-cresol. This is now explicable on the basis of a competitive secondary intra-acyl scission of *m*-tolyl acrylate; it accords with the present results, and with Skraup and Nieten's observations,<sup>6</sup> although the latter workers had recorded nothing which could explain the formation of a styrene from the ester (V).

Formally, the C<sup>2</sup> reaction requires scission of the ester molecule at two points, with combination of the two terminal fragments (alkenyl and aryl); and it is difficult to visualise this as occurring except *via* a free-radical mechanism. Nevertheless, none of the arbitrarily chosen inhibitors listed in Table 2 has any significant effect on the extent of the C<sup>2</sup> reaction, and for the present it is preferred not to suggest any detailed mechanism for the decarboxylation.

*Other Competitive Routes.*—Formation of a little polymerised acrylate (III) calls for no special comment; and the observed traces of alkene in the gaseous pyrolysates may be

<sup>11</sup> Filachione, Lengel, and Fisher, *J. Amer. Chem. Soc.*, 1944, **66**, 494.

<sup>12</sup> Filachione, Lengel, and Ratchford, *ibid.*, 1950, **72**, 839.

accounted for by the tentative free-radical mechanism outlined. Separate pyrolyses of phenyl formate, styrene, and  $\alpha$ -methylstyrene under the same conditions (Table 1, runs 5—7) show that secondary breakdown of these primary products is not responsible *per se* for any of the other minor components of the pyrolysate, or for tar formation.

Skraup and Beng<sup>13</sup> have recorded the thermal Fries-type rearrangement of phenyl  $\beta\beta$ -dimethylacrylate to *o*- $\beta\beta$ -dimethylacryloylphenol, which suggests that the acrylate and  $\alpha$ -methylacrylate might rearrange analogously to the corresponding *o*-acryloyl- or *o*- $\alpha$ -methylacryloyl-phenol. Some evidence for this has been found, though it is not conclusive. A very minor fraction was obtained (Table 1, runs 1—4) which in each case showed both ketonic and phenolic properties: neither this nor its derivatives could be isolated rigorously pure, but it yielded a trace of a crude 2:4-dinitrophenylhydrazone which in its purest form gave (like the parent fraction itself) the colour reactions of a phenol.

Filachione *et al.*<sup>12</sup> found that the pyrolysate from the ester (V; Ar = *m*-tolyl or *p*-chlorophenyl) contained a little diacetyl. This  $\alpha$ -diketone has not been found in the pyrolysate from phenyl acrylate (indeed, this was hardly to be expected), and the conclusion is that it must arise *via* a competitive primary route in the pyrolysis of the ester (V) itself. This view is confirmed by the isolation<sup>14</sup> of an  $\alpha$ -diketone in the pyrolysate from several other  $\alpha$ -substituted esters, an observation which will be more fully described in a later paper.

#### EXPERIMENTAL

*Apparatus and Procedure.*—These have been described previously.<sup>4</sup> The free unpacked space in the reaction vessel was 220 ml., except in run 12 (Table 2). Before each run, carbonised deposits from the previous run were thoroughly removed by heating the vessel to 500° in a current of air, in order to minimise catalytic effects of the type described by Bailey *et al.*<sup>15</sup>

*Preparation of Pyrolysands.*—*Phenyl acrylate.* Acryloyl chloride, prepared<sup>16</sup> from acrylic acid and benzoyl chloride, was treated with phenol in the presence of a little quinol. The crude phenyl ester was fractionally distilled over copper turnings immediately before use (yield *ca.* 65%, b. p. 87—94°/12 mm.,  $n_D^{20}$  1.523; Filachione *et al.*,<sup>11</sup> b. p. 87—94°/12 mm.,  $n_D^{20}$  1.520).

*Phenyl  $\alpha$ -methylacrylate.* This was prepared on the same lines as the acrylate (yield *ca.* 60%, b. p. 98—102°/12 mm.,  $n_D^{20}$  1.515; Filachione *et al.*,<sup>12</sup> b. p. 47—50°/0.2 mm.,  $n_D^{20}$  1.5147; Du Pont,<sup>17</sup> b. p. 83—84°/4 mm.).

*Phenyl formate.* This was prepared as described by Adickes *et al.*,<sup>8</sup> intensive fractionation under reduced pressure leading to pure material (yield *ca.* 10%, b. p. 82—83°/15 mm.) showing negative colour tests for free phenol.

*Styrene and  $\alpha$ -methylstyrene.* Commercial styrene (British Drug Houses Ltd.) and  $\alpha$ -methylstyrene (L. Light & Co. Ltd.) were carefully fractionated, and products with b. p. 146° and b. p. 162° respectively were used for pyrolysis.

*Results.*—Table 1 summarises the overall conditions and results for 7 runs; all gas analyses (*b*) are reported on a nitrogen-free basis. A satisfactory reproducibility is indicated by comparison of runs 1 and 2, and of runs 3 and 4; but the weights of the various fractions are subject to an estimated error of  $\pm 10\%$  owing to manipulative difficulties in purifying small quantities of pyrolysate, and a high degree of accuracy is therefore not claimed for the figures in Tables 1 and 2. In run 12, copper exhibited a promoting rather than an inhibiting effect on the overall pyrolysis; and after this run the walls of the Pyrex-glass reaction vessel were strongly stained with a uniform clear copper-brown colour, which could not be removed by heating at 500° in a current of air or by treatment with mineral acid.

*Analysis.*—The liquid pyrolysates (*a*) were fractionally distilled, to recover and determine unchanged pyrolysand. The remaining major components were characterised as follows,

<sup>13</sup> Skraup and Beng, *Ber.*, 1927, **60**, 942.

<sup>14</sup> Jones and Ritchie, unpublished observation.

<sup>15</sup> Bailey and Rosenberg, *J. Amer. Chem. Soc.*, 1955, **77**, 73; Bailey and King, *ibid.*, p. 75; Bailey, Hewitt, and King, *ibid.*, p. 357.

<sup>16</sup> Stempel, Cross, and Mariella, *ibid.*, 1950, **72**, 2299; Brown, *ibid.*, 1938, **60**, 1325.

<sup>17</sup> Du Pont, *Ind. Eng. Chem.*, 1936, **28**, 1160.

all solid products (or derivatives) being identified by mixed m. p.: (i) Phenol as benzoate; (ii) styrene (b. p. 146°) as 1': 2'-dibromoethylbenzene; (iii)  $\alpha$ -methylstyrene (b. p. 162°) as 1': 2'-dibromo-1'-methylethylbenzene, b. p. 115–125°/8 mm. (Grignard,<sup>18</sup> b. p. 115°/8 mm.), and by oxidation (permanganate) to acetophenone (2 : 4-dinitrophenylhydrazone); (iv) phenyl

TABLE 1. *Pyrolysis of esters (III; R = H or Me) and related substances (550°).*

Pyrolysand	(III; R = H)	(III; R = Me)	Phenyl formate	Styrene	$\alpha$ -Methylstyrene
Run no. ....	1	2	3	4	5
Feed-rate (g./min.) .....	0.33	0.38	0.28	0.30	0.36
Contact time (sec.) .....	88	76	113	106	66
Wt. pyrolysed (g.) .....	69	60	43	48	52
(a) Liquid pyrolysate (g.) ...	66	55	38	42	39
Pyrolysand unchanged (%) ..	48	49	49	54	Trace
(b) Gaseous pyrolysate (l.) ...	3.2	2.2	3.2	3.5	10.4
Composition (%) of (b) :					
CO .....	62.0	58.8	55.2	50.1	99.5
CO <sub>2</sub> .....	23.2	23.2	38.1	40.9	Trace
Unsat. hydrocarbons .....	14.8	18.0	6.7	9.0	Nil
Pyrolysand destroyed [g. (mol.)] .....	36(0.24)	31(0.21)	22(0.14)	22(0.14)	52(0.42)
Intra-acyl scission products [g. (mol.)] :					
PhOH .....	13.1(0.14)	10.0(0.11)	6.8(0.07)	6.0(0.07)	39.0(0.42)
CO .....	2.3(0.08)	1.6(0.06)	2.8(0.08)	2.1(0.08)	12.3(0.44)
CH <sub>2</sub> :CR .....	0.5(0.02)	0.4(0.02)	0.4(0.02)	0.5(0.02)	—
Phenyl formate .....	Trace	Trace	Trace	Trace	Trace
Decarboxylation products [g. (mol.)] :					
CH <sub>2</sub> :CRPh .....	2.9(0.03)	2.2(0.02)	2.6(0.02)	3.3(0.03)	—
CO <sub>2</sub> .....	1.4(0.03)	1.0(0.02)	2.4(0.05)	2.7(0.06)	—
Other products (g.) :					
Carbonised material .....	14.5	13.9	4.6	5.2	—
(IV; R = H or Me) .....	Trace	Trace	Trace	Trace	—
Acylphenol (?) .....	Trace	Trace	Trace	Trace	—
Alkene .....	Trace	Trace	Trace	Trace	—
Polymer .....	0.9	1.0	1.4	1.6	—

TABLE 2. *Effect of free-radical inhibitors on pyrolysis of phenyl acrylate (550°).*

Inhibitor	None	Quinol	Phenanthra-quinone	4-tert.-Butylcatechol	Benzoquinone	Copper
Run no. ....	1—2*	8 †	9 †	10 †	11 †	12 †
Feed-rate (g./min.) .....	0.36	0.35	0.34	0.30	0.30	0.32
Contact time (sec.) .....	82	83	85	97	97	110
Gaseous pyrolysate (l./g. of pyrolysand) .....	0.04	0.02	0.07	0.09	0.11	0.17
Ester unchanged (%) .....	48.5	91	74	63	33	22
Intra-acyl scission (%) .....	28	Nil	9	15	28	29
Decarboxylation (%) .....	7	7	3	9	11	10
Polymerisation (%) .....	2	Nil	6	5	6	6
Carbonisation (%) .....	15	2	8	8	22	33

\* Figures represent average of the concordant runs 1 and 2 (Table 1).

† Inhibitor (1%) dissolved in pyrolysand.

‡ Reaction vessel packed with copper turnings instead of Pyrex-glass rings; free unpacked space 270 ml.

formate (b. p. 173° decomp.) by infrared absorption, and by preparation of formanilide from its hydrolysis product; (v) naphthalene (m. p. 78°) by mixed m. p.; (vi) 2 : 3-dimethylnaphthalene (m. p. 100°) by mixed m. p. [Found : C, 92.8; H, 7.8; *M* (cryoscopic in benzene), 150. Calc. for C<sub>12</sub>H<sub>12</sub> : C, 92.3; H, 7.7%; *M*, 156]; (vii) acetylene by infrared absorption; (viii) methylacetylene by infrared absorption (no evidence for any isomerisation to allene).

Distillation of (a), runs 1 and 2, gave a small oily fraction *A*, b. p. ca. 118°/10 mm. : distillation of (a), runs 3 and 4, gave a similar small fraction *B*, b. p. ca. 130°/10 mm. *A* and *B* both

<sup>18</sup> Grignard, *Compt. rend.*, 1902, **134**, 845.

gave the colour reaction (ferric chloride) of a phenol and both yielded a trace of a 2 : 4-dinitrophenylhydrazone (giving the phenol colour reaction) which could not be obtained rigorously pure. The 2 : 4-dinitrophenylhydrazones had m. p. 239—240° (Found : N, 21.6. Calc. for  $C_{15}H_{12}O_5N_4$  : N, 17.1%) and m. p. 254° (Found : C, 54.0; H, 3.8. Calc. for  $C_{16}H_{14}O_5N_4$  : C, 56.1; H, 4.1%), respectively.

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