

of the starting material) melting at 100.5–100.7° alone and when mixed with the original material.

### Summary

1. *cis*-1,2-Dimethylcyclopentanediol-1,2 undergoes the pinacol rearrangement with migration of a methyl group and production of 2,2-dimethylcyclopentanone.

2. *trans*-1,2-Dimethylcyclopentanediol-1,2 when boiled with dilute aqueous acid undergoes resinification. It has not been possible to char-

acterize any product from this reaction. It is suggested that dehydration without rearrangement is here occurring, yielding a product which is rapidly polymerized by the acid.

3. These observations confirm the conclusion previously reached that in the pinacol rearrangement elimination of a hydroxyl group and the arrival of a migrating radical occur on opposite sides of the same carbon atom.

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## The Pyrolysis of Esters

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Although much is known about the pyrolysis of esters, most of the evidence is fragmentary. To supply additional information of a critical nature seven esters were selected for detailed study. These were ethyl, phenyl, *i*-propyl, *i*-butyl, and *t*-butyl acetates and methyl and ethyl phenylacetates.

The known facts concerning simple esters may be summarized briefly. If a  $\beta$ -H is present in the alkyl portion of the ester,  $\text{RCOOCR}_2\text{CHR}_2$ , the decomposition into acid ( $\text{RCOOH}$ ) and olefin ( $\text{R}_2\text{C}=\text{CR}_2$ ) is general. This was established by Oppenheim and Precht<sup>1</sup> for ethyl acetate and was confirmed recently by Bilger and Hibbert.<sup>2</sup> The latter investigators also extended the reaction (470–500°, 1.2 sec. contact time) to several other esters which included not only the propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl and  $\beta$ -chloroethyl acetates but also the ethyl esters of benzoic, formic, butyric and chloroacetic acids. In their work an unsuccessful search was made for aldehydes among the reaction products, the reagent being a solution of *p*-nitrophenylhydrazine in acetic acid. Bilger and Hibbert noted that methyl and benzyl esters (of acetic and benzoic acids) did not decompose under conditions which caused breakdown of the other esters.

The decomposition products of methyl phenylacetate (sealed tube at 360°) have been reported<sup>3</sup> to be toluene, methane, methanol and oxides of

carbon. Methyl acetate,<sup>4</sup> at 1100°, has been found to change into acetic acid, formaldehyde and acetaldehyde (or their decomposition products) and ethylene.

Five of the esters studied in the present investigation possessed a  $\beta$ -H on the alkyl group. Greatest instability was noticed when this alkyl was tertiary as in *t*-butyl acetate. It decomposed even at 360°. Secondary alkyl (*i*-propyl acetate) exhibited intermediate stability. Greatest stability was noticed when the alkyl was primary (ethyl or *i*-butyl acetates, ethyl phenylacetate).

Nearly equivalent amounts of acetic acid and isobutylene were observed from *t*-butyl acetate at 360–430° and no other products were found. Also, no products other than ethylene and phenylacetic acid (formed in equivalent amounts) were obtained from ethyl phenylacetate at 435–545°. At 625°, however, the latter gave rise to small amounts of toluene and carbon dioxide which were formed obviously from phenylacetic acid by secondary decomposition. The percentage yields of products based on the ester decomposed were found to be as follows: phenylacetic acid 58, toluene 22, carbon dioxide 21, ethylene 78.

The acetic acid and propylene from *i*-propyl acetate were formed in nearly equimolar amounts, but small amounts of acetaldehyde (4%), acetone (3%) and carbon monoxide (12%) were also observed in an experiment at 460°.

Ethyl acetate yielded acetic acid and ethylene in approximately equivalent amounts as expected, but the presence of other products was established

(1) Oppenheim and Precht, *Ber.*, **9**, 325 (1876); Burns, Jones and Ritchie, *J. Chem. Soc.*, 400 (1935).

(2) Bilger and Hibbert, *THIS JOURNAL*, **58**, 823 (1936).

(3) Engler and Löw, *Ber.*, **26**, 1440 (1893).

(4) Peytral, *Bull. soc. chim.*, **31**, 118 (1922).

definitely. These substances were identified in an experiment at 550° (% yields): acetic acid 82, ethylene 83, acetaldehyde 9, formaldehyde 6, acetic anhydride 0.5, methane 8, hydrogen 4, carbon monoxide 1, and a trace of ketene. Similarly, isobutyraldehyde (but not acetaldehyde or formaldehyde), carbon monoxide and methane were found in the products from *i*-butyl acetate, but of course the chief products were acetic acid and isobutylene.

It was established that the olefin from both *t*- and *i*-butyl acetates was isobutylene, unadmixed with isomers. This was determined carefully because *i*-butyl acetate,  $\text{Me}_2\text{CH}-\text{CH}_2-\text{OAc}$ , bears a structural resemblance to 1,1-diphenyl-2-chloroethane,  $\text{Ph}_2\text{CH}-\text{CH}_2-\text{Cl}$ , which is known to pyrolyze<sup>5</sup> into hydrogen chloride and stilbene,  $\text{PhCH}=\text{CHPh}$ . Were isobutyl acetate to behave analogously, one would anticipate 2-butene as the olefin of the reaction, but only 2-methylpropene (isobutylene) was found.

Phenyl acetate and methyl phenylacetate were much more stable than the other esters. At either 435 or 535° practically no change occurred, but at 625° there was decomposition. Evidently, therefore, an interval of about 200° separates the decomposition temperatures of the two groups. Phenyl acetate pyrolyzed smoothly into ketene and phenol. The yield of ketene at 625° was 84%.



The decomposition of methyl phenylacetate was much more complex. The products formed in greatest amounts were carbon monoxide, benzaldehyde and toluene, but other products included hydrogen, ethylene, methane, formaldehyde, carbon dioxide, water and an organic acid. Formaldehyde, which is known to decompose rapidly above 500°, may have been the precursor of much of the carbon monoxide and hydrogen, and probably much of the hydrogen was consumed at the high temperature. The striking product of the reaction was benzaldehyde. The carbonyl group in it is attached to the aromatic nucleus, whereas the carbonyl group in the ester is separated from the nucleus by a methylene group. Evidently, therefore, something more complex than a simple splitting must have occurred to have caused the formation of benzaldehyde.

These average percentage yields of products were formed, based on the ester which was decomposed. The experiments were performed

(5) Hepp, *Ber.*, **6**, 1439 (1873).

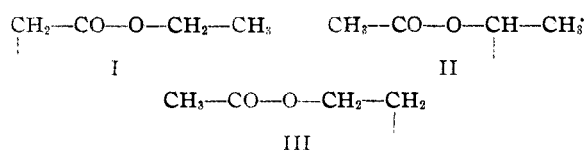
at 625° and about five seconds contact time: benzaldehyde 71, toluene 49, carbon monoxide 92, formaldehyde 25, ethylene 29, hydrogen 27, methane 15, carbon dioxide 12 and an organic acid 4. The benzaldehyde and toluene were isolated directly and, therefore, represent minimum values.

**Mechanisms.**—No single mechanism accounts for the facts adequately, and three processes seem to be involved. One of them is the chain mechanism, with univalent radicals as intermediates, but it cannot apply, except in small measure, to the esters which possess a  $\beta$ -hydrogen. A few considerations will make this evident.

If the chain mechanism is applied to *t*-butyl acetate, the predicted products include not only isobutylene and acetic acid but also ketene (or acetic anhydride, from ketene and acetic acid), acetone and methane. Since this mechanism calls for five products instead of two, it is obviously inadequate.

Similar reasoning shows that the chain mechanism cannot serve in the pyrolysis of ethyl phenylacetate since, besides ethylene and phenylacetic acid, it would require the production of formaldehyde, methane, phenylketene, toluene, carbon monoxide and acetaldehyde. None of the last six compounds was formed in experiments at 435–545°.

The steps with ethyl acetate will be taken up in detail. With the chain mechanism, interaction of a radical R with  $\text{CH}_3\text{COOCH}_2\text{CH}_3$  would yield RH and residues I, II or III.



Breakdown of I should lead to formaldehyde, ketene (or acetic anhydride), and methane:  $\text{I} \longrightarrow \text{CH}_2=\text{C}=\text{O} + -\text{O}-\text{CH}_2-\text{CH}_3 \longrightarrow \text{O}=\text{CH}_2 + \text{CH}_3-$ . In previous work with ethyl acetate, the presence of formaldehyde and methane among the pyrolytic products has escaped detection, but the "odor of ketene" has been noticed.<sup>6</sup> Breakdown of II should yield acetaldehyde, carbon monoxide and methane:  $\text{II} \longrightarrow \text{CH}_3- + \text{CO} + \text{O}=\text{CH}-\text{CH}_3$ . III should give rise to ethylene and acetic acid:  $\text{III} \longrightarrow \text{CH}_3-\text{CO}-\text{O}- + \text{CH}_2=\text{CH}_2$ .

(6) Stewart and Wilmore, *Nature*, **75**, 510 (1907); Wilmore, *J. Chem. Soc.*, **91**, 1939 (1907).

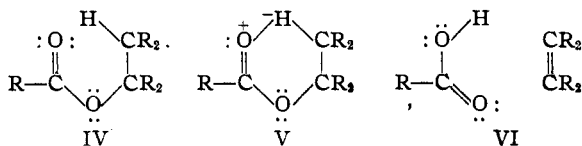
Possibly the aldehydes which were produced did come via I and II but, if so, it seems obvious that no more than a small fraction of the observed acetic acid should come via III because the yields of I, II and III should be comparable. The bulk of the acetic acid, therefore, requires another mechanism to account for it.

As was mentioned earlier, ethyl acetate is more stable than *t*-butyl acetate. The temperature required for pyrolysis of the latter was so low that scission into radicals appeared to be completely inhibited. With the higher temperature required for the decomposition of ethyl acetate the breakdown into radicals was starting to be a factor, although not yet one of importance.

A similar situation exists with *i*-propyl and *i*-butyl acetates. Compounds predicted by the chain mechanism are observed but they comprise only a small portion of the products.

**Cyclic Hydrogen Bridge.**—The concept of hydrogen bonds or hydrogen bridges<sup>7</sup> has been developed in recent years to explain such facts as the association of water or hydrogen fluoride, the weakness of carboxylic acids, the weakness of ammonium hydroxide and many other facts, all of which, however, have been low temperature phenomena. The concept seems applicable also to some high temperature processes and it is proposed that the esters which require only moderately high temperatures for their pyrolysis break down by a mechanism involving hydrogen bridges.

Esters which possess a  $\beta$ -H in the alkyl group (IV) may undergo a chelate type of 6-atom ring closure by way of a hydrogen bridge (V). Re-adjustment of the electrons would give rise to acid and olefin (VI).



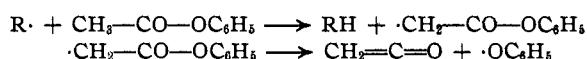
Methyl esters cannot change into 6-atom rings comparable to V, which may account for their greater stability.

When hydrogen bridges occur in stable structures, negative atoms are involved on both sides of the bridge (such as O-H-O, or O-H-N or F-H-F). The O-H-C bridge has not been observed at ordinary temperatures, but it is rea-

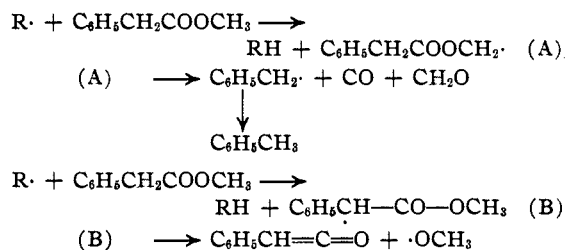
sonable to assume for it a transient existence at elevated temperatures. Also, because oxygen is more negative than carbon, hydrogen should remain with the oxygen when this bridge is broken.

This mechanism calls for only moderately high temperatures. Ethyl phenylacetate, which yielded only ethylene and phenylacetic acid at 435°, was studied at 545 and 625° to see if the mechanism was changed at higher temperatures. No such change was found for no aldehydes were produced. The temperature of 625° is sufficient in some cases to initiate C-C scission with the formation of radicals, but apparently the only effect of the increased temperature in this reaction was to increase the velocity of the original process.

**Radicals as Intermediates.**—The chain reaction mechanism may account for the pyrolysis of phenylacetate, since the products obtained, namely, ketene and phenol, are those predicted by the theory.



When a similar mechanism is applied in its simplest form to methyl phenylacetate the products predicted include toluene, carbon monoxide, formaldehyde and hydrogen, all of which were found. Phenylketene was indicated also but was not found. This is not surprising in view of its instability. The steps are as follows



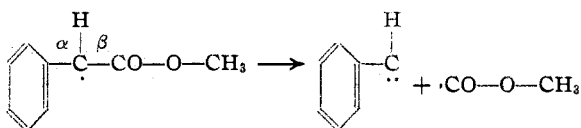
The  $\cdot OCH_3$  radical may change to methanol (RH, in the equation), or to hydrogen and formaldehyde. With methanol, phenylketene would regenerate methyl phenylacetate.

**Methylene Radicals as Intermediates.**—The above mechanism for methyl phenylacetate is not self-sufficient because it fails to account for the most important product of the reaction, namely, benzaldehyde. Its production may be explained satisfactorily by assuming that phenylmethylene is an intermediate radical. In the pyrolysis of methane, which calls for severe thermal conditions, the methylene radical is

(7) For a review of the material, see Huggins, *J. Org. Chem.*, 1, 407 (1937).

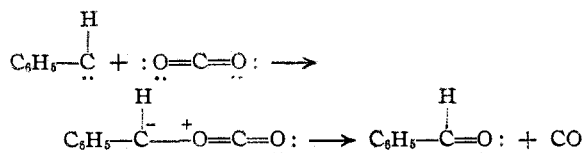
thought by Kassel<sup>8</sup> to be a fundamental intermediate. Storch and Kassel<sup>9</sup> also favor it as an intermediate in the pyrolysis of ethane, but they point out that a chain reaction which involves univalent radicals proceeds concurrently.

With methyl phenylacetate, it is proposed that radical B, because of high temperature and structural weakness, breaks as follows



The C-C bond which undergoes scission is beta to the unsaturation of the phenyl nucleus and, therefore, possesses an instability<sup>10</sup> not found in the acetic esters. The resulting carbomethoxyl radical may break into  $\text{CO} + \cdot\text{OCH}_3$  or into  $\text{CO}_2 + \cdot\text{CH}_3$ .

The phenylmethylene radical, possessing as it does only six electrons on the carbon atom, must attach itself to neighboring unshared electrons to create the necessary octet. Most probably, these unshared electrons would come from some oxygen-containing substance, as the original ester, or carbon dioxide, etc. The oxygen atom which is attracted to the carbon atom in this way is the one which appears as benzaldehyde. This may be illustrated most simply with carbon dioxide as the source of the oxygen, but a similar plan would follow for other compounds.



The fact that a much higher decomposition temperature was required for the breakdown of methyl phenylacetate than for ethyl phenylacetate explains why benzaldehyde was not formed in the latter case. Obviously, a formidable energy barrier must be hurdled to bring about this effect.

The fact that several mechanisms are involved in the pyrolysis of esters suggests that several mechanisms may be involved also in the pyrolysis of compounds in other series, particularly if sizeable temperature differences are involved in initiating the breakdown. Most of the earlier thought on this subject has presumed that one

type of mechanism alone was adequate for a particular series if not for all series.

### Experimental Part

**Substances Used.**—The following esters were washed, dried and closely refractionated before use: ethyl acetate, b. p. 77.0–77.1°; phenyl acetate, b. p. 96.5–96.6° at 30 mm.; methyl phenylacetate, b. p. 214° (735 mm.), sapon. equiv., 150. Hydrolysis of the last of these yielded phenylacetic acid, m. p. 74–75°, free from benzoic acid.

For some of the runs, methyl phenylacetate and ethyl phenylacetate were synthesized from pure phenylacetic acid, m. p. 75.5–76.0°. The latter was dissolved in anhydrous methanol or ethanol which contained dry hydrogen chloride and the mixture was refluxed for eight hours. The esters were separated and purified in the usual way. After two distillations at 65 mm. the methyl ester was collected at 137.0–137.1° (yield 90%), and the ethyl ester at 141–142°.

Synthetic *i*-propyl acetate was used in all the runs. The *i*-propyl alcohol was thrice distilled through an efficient column. The fraction obtained, b. p. 82.5–82.6°, was shown by oxidation with dichromate to contain less than 0.1% of *n*-propyl alcohol. About 1% of concd. sulfuric acid was added to 9 moles of the alcohol and an equimolar quantity of pure acetic anhydride was added at such a rate as to maintain refluxing. Then the reaction mixture was cooled, the ester salted out and neutralized with sodium bicarbonate, washed with water and dried over calcium chloride. An 80% yield of *i*-propyl acetate, b. p. 89.4–89.5°, was obtained.

The *i*-butyl acetate was made from carefully fractionated *i*-butyl alcohol, b. p. 107.1–107.2°. Esterification of this alcohol with acetic anhydride, or with refluxing glacial acetic acid in the presence of a little hydrogen chloride or *p*-toluenesulfonic acid, yielded *i*-butyl acetate which boiled at 118.1–118.2°.

*t*-Butyl acetate was prepared from *t*-butyl alcohol (distilled from sodium), acetic anhydride and a little zinc chloride according to the method of Norris and Rigby.<sup>11</sup> The yields were only 48–50%, but the purity was excellent (b. p. 97.4–97.6°).

**Apparatus.**—The esters were introduced into the top of a vertical Pyrex reaction tube by displacement with mercury. In most runs, a 15-cm. electric furnace was used but in some runs it was replaced by a 30-cm. furnace. The temperature was controlled and recorded by a chromel-alumel thermocouple attached to a Leeds and Northrup recorder-controller. The glass-encased thermocouple was placed in the middle of the reaction tube.

An iced receiver was attached to the bottom of the reaction tube and it in turn was connected to a low-pitched spiral reflux column which was cooled by ice-salt. This served to condense all of the higher boiling products as well as the undecomposed ester. The uncondensed vapors from ethyl acetate were then passed through a second receiver at –80° to collect formaldehyde, acetaldehyde or ketene. The same was used with *i*-propyl, *i*-butyl and *t*-butyl acetates but in these runs no appreciable quantity of liquid was condensed. The remaining gas was passed to a gas-collecting bottle over salt water. With methyl

(8) Kassel, *THIS JOURNAL*, **57**, 833 (1935).

(9) Storch and Kassel, *ibid.*, **59**, 1245 (1937).

(10) Hurd and Bollman, *ibid.*, **55**, 699 (1933); **56**, 447 (1934).

(11) Norris and Rigby, *ibid.*, **54**, 2088 (1932).

phenylacetate, the second trap contained water at 3° to collect formaldehyde. In runs with the acetic esters an aniline trap or a trap containing standard alkali was inserted between the second receiver and the bottle, to absorb ketene.

#### Analytical Methods

**Qualitative.**—Qualitative tests for formaldehyde, acetaldehyde and ketene were performed to precede the quantitative experiments. Formaldehyde was identified as methylenedi- $\beta$ -naphthol. For this purpose, one-third of the products (diluted with water) from the second receiver from the ethyl acetate experiments was mixed with 10 cc. of alcohol, 2 cc. of dilute hydrochloric acid and 1 g. of  $\beta$ -naphthol. After heating for fifteen minutes and cooling, 0.5 g. of the derivative, m. p. 204°, was obtained. Formaldehyde was identified similarly in the products of the second receiver from methyl phenylacetate.

To identify acetaldehyde from ethyl acetate, a portion of the solution in the second receiver was neutralized with dilute sodium hydroxide and distilled. The distillate, diluted with water, responded positively to the fuchsin test. It was oxidized with chromic acid and the volatile acid removed by distillation. The latter was neutralized by sodium hydroxide and evaporated to dryness. The sodium acetate in the residue was converted to *p*-bromophenacyl acetate, m. p. 85°, on treatment with *p*-bromophenacyl bromide. Acetaldehyde was detected qualitatively in like manner from the low-boiling products of the first receiver with *i*-propyl acetate.

Direct evidence for ketene was obtained in the run at 525° with ethyl acetate by inserting a trap containing 20 cc. of aniline between the second receiver and the gas-collecting bottle. In working up the products, any acetic acid was extracted by sodium bicarbonate solution.<sup>12</sup> The water solution was ether-extracted and the extract was placed with the aniline. The ether and aniline were distilled off and the residue was extracted with boiling water. About 0.1 g. of acetanilide, m. p. 113°, separated on cooling. A trace of ketene was revealed similarly in runs with *i*-propyl and *i*-butyl acetates. With phenyl acetate it was the chief product.

That the liquid products from the pyrolysis of phenyl acetate contained phenol was established readily by distillation. The fraction which was collected at 179–182° reacted strongly with ferric chloride and gave an  $\alpha$ -naphthylurethan, melting at 132°.

The gas from the first receiver and its attached spiral condenser was treated in three different ways. For a time in the first run it was passed into a trap containing 45 cc. of water. Then it was passed into a trap containing 20 cc. of aniline. In the second run, it was passed into an empty trap at -78° which was connected to an aniline trap.

The water in the first trap was free from aldehydes (Schiff reagent). From the aniline traps, acetanilide was isolated in quantity (m. p. 113.5°). No gaseous product was obtained in either run. At the end of the second run, about 1 cc. of ketene had collected in the trap at -78°. When this was vaporized and passed into the aniline, there was no residual acetylketene. The yield

of ketene was calculated from the weight of acetanilide isolated.

The liquid products consisted only of phenyl acetate and phenol. The former was determined by acetyl analysis,<sup>13</sup> and the latter by bromate-bromide titration.<sup>14</sup> To analyze for phenol in the presence of phenyl acetate, it was found that phenyl acetate underwent quantitative hydrolysis into phenol on refluxing for thirty minutes with sodium ethoxide solution. Therefore, the mixture of phenyl acetate and phenol was subjected to this hydrolysis prior to the bromate-bromide titration. Since the ester content was known, that portion of the phenol which came from the ester was computed readily.

The qualitative presence of acetone in the liquid products (first receiver) from *i*-propyl acetate was established by neutralizing a portion of it and treating that part which boiled below 80° with semicarbazide hydrochloride and sodium acetate. After standing, 0.5 g. of acetone semicarbazone, m. p. 189–190°, was obtained. No acetone was detected from *t*-butyl acetate.

Acetic acid was identified by boiling point and by its derivative, *p*-bromophenacyl acetate, m. p. 85°. No more than traces of acetic anhydride were present by quantitative determination (below).

No allyl acetate was found by distillation of the products from *i*-butyl acetate. The fraction boiling from 85–116° revealed no ester for no alkali was consumed by saponification test, but it contained much isobutyraldehyde for it gave a strong fuchsin test and yielded a 2,4-dinitrophenylhydrazone, m. p. 182°.

A slight fuchsin test was obtained in the products from the 625°-run of ethyl phenylacetate, but otherwise all tests for aldehydes were negative. Phenylacetic acid and toluene (only from the run at 625°) were identified by direct isolation. The toluene was confirmed as 2,4-dinitrotoluene, m. p. 70°. Water, toluene and benzaldehyde (b. p. 177–183°, semicarbazone m. p. and mixed m. p. 222°) from methyl phenylacetate were isolated directly. No evidence was secured for phenylacetaldehyde, and the trace of acid observed could not be isolated for characterization.

Data summarizing both the qualitative and quantitative data of some representative runs are collected in Table I.

**Quantitative.**—Quantitative determinations on the various products were carried out volumetrically. The acid content was determined by direct titration on an aliquot portion of the products with standard sodium hydroxide. The ester content was determined on another portion by saponification, using a known amount of standard alkali and back titration with dilute standard sulfuric acid. The acetic anhydride was determined on an aliquot portion by means of the reaction with anhydrous pyridine and oxalic acid,<sup>15</sup> the volume of carbon monoxide and carbon dioxide evolved being indicative of the anhydride content.

The total aldehyde content of both receivers was determined on aliquot portions by oxidation with 0.1 *N* potassium dichromate solution and sulfuric acid. It was necessary to correct this value in the ethyl acetate experi-

(13) Freudenberg, *Ann.*, **433**, 280 (1923).

(14) Francis and Hill, *This Journal*, **46**, 2498 (1924).

(15) Whitford, *ibid.*, **47**, 2939 (1925).

(12) Hurd and Martin, *This Journal*, **51**, 3615 (1929).

TABLE I  
 PYROLYSIS OF SEVEN ESTERS

Ester	Ethyl acetate			<i>i</i> -Propyl acetate			<i>t</i> -Butyl acetate	<i>i</i> -Butyl acetate		Phenyl acetate		Ethyl phenylacetate				Methyl phenylacetate			
	1	2	3	1	2	3	1	1	2	1	2	1	2	3	4	1	2	3	4
Run no.	98	136	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150
Vol. of tube, cc.	525	550	430	430	460	360	420	650	625	645	435	485	545	625	535	625	625	625	625
Temp., °C.	489	440	35	130	95	12	68	120	26	53	25	28	28	33	41	38	35	51	51
Duration, min.	14.8	53.5	3.9	20.3	17.9	2.6	7.6	27.4	7.0	14.3	7.7	8.7	8.8	7.7	6.8	4.8	5.2	6.6	6.6
Contact time, sec.	3.00	1.00	1.00	1.00	0.90	0.77	1.52	0.56	0.485	0.485	0.539	0.445	0.439	0.503	0.69	1.00	0.69	1.00	1.00
Bater taken	289.5	96.5	117	117	105	100	203	56	61	61	86	71	70	80	100	145	100	145	145
Gas formed (STP), liters	47.95	19.50	2.10	6.10	10.35	0.38	3.9	9.0	...	...	0.90	1.30	4.70	9.60	1.1	6.18	4.41	7.02	7.02
Extent of decn., %	63.7	90.1	18.9	37.7	55.0	2.70	13.6	98.1	12.7	24.8	8.3	17.3	56.0	85.2	0.87	15.0	16.9	18.5	18.5
Vol. of liquid products, cc.	215.5	55.0	110	100	78.0	97	194	30	59.5	57.3	85	70	60	36.5	99.5	140	94	135.5	135.5
Gas analysis, % by vol.																			
CO <sub>2</sub>	1.31	1.53	...	...	...	...	...	...	...	...	...	...	...	21.42	...	5.66	5.32	6.95	6.95
C <sub>2</sub> H <sub>4</sub>	85.80	85.53	...	...	...	...	...	...	...	...	100.0	100.0	100.0	78.58	...	15.62	14.97	19.71	19.71
H <sub>2</sub>	4.74	3.95	...	...	...	...	...	...	...	...	...	...	...	...	...	18.96	15.30	12.50	12.50
CO	1.31	0.66	5.00	4.15	1.83	...	2.68	10.20	...	...	...	...	...	...	...	53.10	56.55	49.45	49.45
CH <sub>4</sub>	6.84	8.33	13.86	10.65	12.84	...	10.76	6.40	...	...	...	...	...	...	...	6.66	7.82	11.39	11.39
C <sub>3</sub> H <sub>6</sub>	...	...	81.14	85.20	85.32	...	...	...	...	...	...	...	...	...	...	...	...	...	...
C <sub>4</sub> H <sub>8</sub> (iso)	...	...	...	...	...	100.0	85.56	83.40	...	...	...	...	...	...	...	...	...	...	...
Yield of products, mole per mole decomposed																			
Acetic acid	0.80	0.82	0.507	0.664	0.806	0.86	0.885	0.684	...	...	...	...	...	...	...	...	...	...	...
Acetaldehyde	.032	.097	.169	.122	.042	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Formaldehyde	.081	.064	...	...	...	...	...	...	...	...	...	...	...	...	...	0.21	0.33	0.20	0.20
Acetic anhydride	.010	.004	tr.	tr.	tr.	...	tr.	tr.	...	...	...	...	...	...	...	...	...	...	...
Ketene	tr.	tr.	tr.	tr.	tr.	...	tr.	tr.	0.84	0.63	...	...	...	...	...	...	...	...	...
Acetone	...	...	.275	.066	.028	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Isobutyraldehyde	...	...	...	...	...	...	*	.156	...	...	...	...	...	...	...	...	...	...	...
Phenol	...	...	...	...	...	...	...	...	.89	.98	...	...	...	...	...	...	...	...	...
Phenylacetic acid	...	...	...	...	...	...	...	...	...	...	0.98	0.77	0.82	0.58	...	...	...	...	...
Toluene	...	...	...	...	...	...	...	...	...	...	...	...	...	.22	...	.33	.53	.60	.60
Benzaldehyde	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	.94	.68	.51	.51
Organic acid	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	.044	.047	.032	.032
Carbon dioxide	0.015	0.014	...	...	...	...	...	...	...	...	...	...	...	.21	...	.10	.13	.12	.12
Ethylene	.96	.83	...	...	...	...	...	...	...	...	.89	.75	.85	.78	...	.29	.25	.33	.33
Hydrogen	.053	.038	...	...	...	...	...	...	...	...	...	...	...	...	...	.35	.26	.21	.21
Carbon monoxide	.015	.007	.027	.029	.016	...	.023	.075	...	...	...	...	...	...	...	.97	.96	.84	.84
Methane	.076	.080	.069	.077	.119	...	.092	.047	...	...	...	...	...	...	...	.12	.13	.19	.19
Propylene	...	...	.402	.616	.796	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Isobutylene	...	...	...	...	...	.81	.730	.600	...	...	...	...	...	...	...	...	...	...	...

\* Isobutyraldehyde was established qualitatively by its 2,4-dinitrophenylhydrazone.

ments for the dichromate which was consumed in oxidizing the ester concurrently ( $\text{CH}_3\text{COOC}_2\text{H}_5 \longrightarrow 2\text{CH}_3\text{COOH}$ ). The difference between the total equivalents of dichromate and the equivalents consumed by the ester gave the value for total aldehydes. The procedure was tested on a known mixture of ethyl acetate and acetaldehyde, as follows.

A definite volume of acetaldehyde (capillary pipet) was heated for three hours on the steam-bath with 150.00 cc. of 0.1024 *N* potassium dichromate and sulfuric acid, after which potassium iodide was added. Then, 34.30 cc. of 0.1410 *N* sodium thiosulfate was required. From this 102.77 cc. of 0.1024 *N* dichromate was consumed. Then a mixture of this same quantity of acetaldehyde and 0.050 cc. of ethyl acetate (0.0005 mole) was treated similarly. This time, 122.46 cc. of 0.1024 *N* dichromate was consumed. The difference of 19.69 cc. ( $\approx 2.01$  cc. of 1 *N*) represents 0.002 equivalent, which agrees with the ethyl acetate taken ( $0.0005 \times 4 = 0.002$ ) since four oxidation equivalents are involved in the oxidation of ethyl alcohol to acetic acid.

In a similar manner it was established that the oxidation equivalent for *i*-propyl acetate (*i. e.*, the correction factor) was twice the molecular weight. Thus, there was hydrolysis and oxidation quantitatively to acetone on heating with 0.0789 *N* potassium dichromate and sulfuric acid:  $\text{CH}_3\text{COOCH}(\text{CH}_3)_2 \longrightarrow \text{CH}_3\text{COOH} + (\text{CH}_3)_2\text{CO}$ .

No such corrections were necessary to analyze for isobutyraldehyde from *i*-butyl acetate for it was separated from the ester before oxidation. The benzaldehyde and toluene from methyl phenylacetate were determined by direct distillation analysis.

The acetone content of the products from *i*-propyl acetate was estimated in a manner patterned after the suggestion of Marseo.<sup>16</sup> The aldehyde and ketone both react with a 2% solution of hydroxylamine hydrochloride in water. The aldehyde releases 94.40% of the theoretical amount of hydrochloric acid while 1.00 cc. of 0.1000 *N* sodium hydroxide is required for the hydrochloric acid set free by each 0.0001 mole of acetone. The sample (an aliquot of the liquid products) was neutralized with standard alkali to the methyl orange end-point. Six hundred cc. of 2% hydroxylamine hydrochloride solution was then added. The solution was titrated to near neutrality and allowed to stand for twenty seconds. This process was repeated several times and the mixture was neutralized after one minute of stirring. By a previous knowledge of the acetaldehyde content the acetone content was determined.

The gaseous products were identified and analyzed by absorption methods in a modified Orsat apparatus.<sup>17</sup> The olefin in the gas from *i*-butyl and *t*-butyl acetates was exclusively isobutylene. In both cases the gas dissolved completely in 63% sulfuric acid. This conclusion was confirmed by distillation analysis in a Podbielniak column. No propylene was found. The  $\text{C}_4$ -fraction from the distillation was liquefied and distilled analytically from a Frey-Hepp column<sup>18</sup> with ethylene oxide as a "pusher." There was a long distillation plateau for isobutylene at  $-6^\circ$  but no plateau at a higher temperature for 2-butene.

Methane was the exclusive paraffin in the gas from methyl phenylacetate since  $n$  in  $\text{C}_n\text{H}_{2n+2}$  was found to be 1.0.

The acetic acid was determined quantitatively by direct titration. Analysis of the unused ester with some of the esters called for the use of a solution of sodium ethoxide in ethanol, since aqueous solutions of sodium hydroxide were ineffectual. For example, after an eight-hour period of refluxing of 10 cc. of *t*-butyl acetate and 25 cc. of 28% sodium hydroxide an insoluble layer of ester remained. Distillation of this layer yielded 9 cc., b. p.  $90-96^\circ$ . Correct saponification values for the pure ester (1 cc.) were obtained by refluxing for half an hour with 50 cc. of *N* sodium ethoxide solution and back-titrating with *N* sulfuric acid.

### Summary

*t*-Butyl acetate underwent pyrolysis at  $360^\circ$  to yield acetic acid and isobutylene as exclusive products. Ethyl phenylacetate also underwent this simple type of scission into phenylacetic acid and ethylene at  $435-545^\circ$ .

In the case of ethyl acetate, pyrolysis into acetic acid and ethylene also occurred at temperatures of  $525-550^\circ$ , but smaller quantities of aldehydes and other gases were identified. Likewise, *i*-propyl acetate at  $430-460^\circ$  gave rise not only to acetic acid and propylene but also to significant amounts of acetone, acetaldehyde, carbon monoxide and methane. Also, at either  $420$  or  $650^\circ$ , small amounts of isobutyraldehyde, carbon monoxide and methane were found mixed with the acetic acid and isobutylene produced from isobutyl acetate.

It was demonstrated that no 2-butene was formed during pyrolysis of either *t*- or *i*-butyl acetates.

Phenyl acetate and methyl phenylacetate were much more thermostable than the other five esters. The extent of decomposition was negligible at  $530^\circ$ . At  $625-645^\circ$ , phenyl acetate pyrolyzed smoothly into phenol and ketene. Methyl phenylacetate, at  $625^\circ$ , yielded benzaldehyde, toluene and carbon monoxide in quantity, but formaldehyde, methane, hydrogen, ethylene and carbon dioxide were also formed.

A mechanism involving a cyclic hydrogen bridge is proposed to explain the low-temperature pyrolysis of esters into acid and olefin. The chain reaction mechanism, involving free radicals, cannot account for this process but it becomes important with the thermostable esters. To account for benzaldehyde from methyl phenylacetate, it is suggested that the phenylmethylene radical is an essential intermediate.

(16) Marseo, *Ind. Eng. Chem.*, **18**, 701 (1926).

(17) Hurd and Spence, *THIS JOURNAL*, **51**, 3356 (1929).

(18) Frey and Hepp, *Ind. Eng. Chem.*, **25**, 444 (1933); Hurd and Goldsby, *THIS JOURNAL*, **56**, 1812 (1934).