erizes mostly to 2,3-dimethylpentane, with minor amounts of 2-methylhexane and 3-methylhexane. The main products of triptane isomerization were 2-methylhexane and 2,3-dimethylpentane. These results substantiate the observations of previous investigators that sulfuric acid is a specific catalyst for shifting the methyl group along the hydrocarbon chain and that only such paraffin hydrocarbons which contain tertiary carbon atoms are susceptible to isomerization with this catalyst.

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Summary

The action of concentrated sulfuric acid on various paraffin hydrocarbons indicates that this acid is a satisfactory isomerization catalyst for liquid paraffins containing at least one tertiary carbon atom. In contrast with the action of aluminum chloride, there is only a very small loss of paraffin to the acid layer. Conditions may be chosen so that the major portions of the product are isomers.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DE PAUL UNIVERSITY]

The Pyrolysis of Methyl Phthalate[1]

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This study of the pyrolysis of methyl phthalate was undertaken as part of a program to determine the nature of the materials produced at various temperatures by the thermal decomposition of some common plasticizers. The literature on the subject seems to be meager and, in particular, does not report data concerning the effect of increasing temperature on the nature of the degradation products.

That methyl phthalate is stable at its boiling point is known,[3] but apparently only one attempt has been made to study the products formed when it is heated to the point of decomposition. Meyer and Hofmann[4] pyrolyzed it at a "glowing heat," reported that the products were methyl benzoate (a trace), formaldehyde, methyl biphenyltricarboxylate and methyl biphenyldicarboxylate.

In the present investigations methyl phthalate was pyrolyzed in Sillimanite tubes at temperatures of 400 to 1000° at atmospheric pressure, and without diluents. The amount of decomposition at 405° was small, but at similar rates of delivery (*ca.* 0.4 g./min.) it increased to 36% at 608°. 97% at 805° and was complete at 1000°.

Analysis of the condensable degradation products formed at 405° showed that they consisted of formaldehyde, water (4.6%), phthalic anhydride (28.2%) and unidentified neutral fraction (51.0%).[5] However, at 608° new products appeared and the condensable fraction contained phthalic anhydride (3.4%), benzene (2.7%), toluene (5.6%), xylene (3.7%), methyl benzoate (37.3%) and a neutral, unsaponifiable fraction (5.8%). Increasing the temperature of pyrolysis to 805° produced condensable materials which consisted of only benzene (16.3%), toluene (1.4%) and the unsaponifiable portion (12.1%). At 1000° the condensable fraction (8.7%) was too small to be analyzed by the methods employed. At all temperatures except 1000° formaldehyde was qualitatively identified among the products but quantitative analyses were unsuccessful.

The non-condensable products proved to be a mixture of carbon dioxide, carbon monoxide, hydrogen, methane, acetylene, ethylene and higher olefins. At low temperatures carbon dioxide constituted 93% of the mixture, but as the temperature of pyrolysis increased, this rapidly diminished. Thus, at 1000° carbon monoxide and hydrogen accounted for three-fourths of the gases. These and other data are presented in Tables I and II.

Attempts to separate the components of the high molecular weight unsaponifiable fractions were unfruitful. Only biphenyl could be isolated and identified.

At 405° methyl phthalate is decomposed to phthalic anhydride, probably by the elimination of methyl ether with subsequent decomposition of the latter[6] to formaldehyde and gaseous hydrocarbons in a manner analogous to that found for other ethers.[7,8] However, at 608° the methyl phthalate is decomposed along a different degradation path, probably through methyl *o*-toluate and from this to aromatic hydrocarbons and methyl benzoate.

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[2] Taken in part from a thesis presented by Jerome T. Siedlecki to the Graduate School of De Paul University in partial fulfillment of the requirements for the degree of Master of Science (1949).

[3] Nagel and Abelsdorff, *Wiss. Veroffentlich Siemens-Konzern*, **5**, 193 (1926); *C. A.*, **21**, 1642 (1927).

[4] Meyer and Hofmann, *Monatsh.*, **39**, 109 (1918).

[5] Parenthesized values are percentages by weight of the methyl phthalate decomposed.

[6] Hinshelwood and Askey, *Proc. Roy. Soc.* (*London*), **115A**, 215 (1927).

[7] Hurd and Glass, THIS JOURNAL, **61**, 3490 (1939).

[8] Lachman, *ibid.*, **45**, 2358 (1923).

Table I

Pyrolysis of Methyl Phthalate

Temp., °C.	405	608	805	1000
Charge, g.	203.3	204.6	197.3	92.2
Rate, g./min.	0.407	0.432	0.385	0.364
Products, g.				
Solid	0.0	4.1	19.4	35.8
Liquid	203.0	174.3	63.3	8.0
Gas	0.5	26.3	114.7	48.4
Total	203.5	204.7	197.4	92.2
Products, %				
Solid	0.0	2.0	9.8	38.8
Liquid	99.8	85.2	32.1	8.7
Ester decomposed				
Grams	3.0	73.7	191.0	92.2
Per cent.	1.5	36.0	96.8	100.0
Gases, l. at STP	0.26	20.4	99.7	59.5
Gases, vol. %				
Carbon dioxide	91.5	33.8	25.1	12.7
Acetylene		0.3	0.6	0.8
Propylene +[a]	0.5	0.0	0.0	0.0
Ethylene	5.7	0.0	0.3	0.1
Carbon monoxide	1.2	37.4	38.9	34.9
Hydrogen	0.0	8.1	14.5	40.3
Methane	1.2	20.4	20.6	11.2

[a] Propylene and higher olefins.

Table II

Percentage Composition by Weight of the Degradation Products from Methyl Phthalate

Temp., °C.	405	608	805	1000
Carbon and tars	0.0	5.5	10.1	38.8
Liquid				
Formaldehyde	0.3[a]	0.1[a]	Present	Not present
Water	4.6	0.0	0.0	
Benzene	.0	2.7	16.3	
Toluene	.0	5.6	1.4	
Xylene	.0	3.7	0.0	
Methyl benzoate	.0	37.3	0.0	
Phthalic anhydride	28.2	3.4	0.0	
Unsaponifiable[b]	51.0	5 8	12.1	
Total				8.7[d]
Gases				
Carbon dioxide	15.3	18.4	25.7	16.1
Acetylene	0.0	0.1	0.4	0.6
Propylene +[c]	.1	0.0	0.0	0.0
Ethylene	.5	0.0	0.2	0.1
Carbon monoxide	.1	12.9	25.4	28.2
Hydrogen	.0	0.2	0.7	2.4
Methane	.1	4.0	7.7	5.2

[a] Includes only the amount collected in the water-filled, ketene traps. [b] Unsaponifiable material having a boiling point higher than that of xylene. [c] Propylene plus higher olefins. [d] No analysis was attempted.

Although methyl *o*-toluate was not isolated, the above scheme of degradation was tested by pyrolyzing it at 600°. Fractional distillation of the condensable portion showed that about half of the ester decomposed had been converted to toluene, xylene and methyl benzoate.

At 805° the condensable products obtained from methyl phthalate consisted of toluene and the unsaponifiable mixture of substances more complex than xylene. This is expected since it has been reported that pyrolysis progressively decomposes alkylated benzenes to lower benzene homologs, these to benzene, and this in turn to diphenyl and polynuclear hydrocarbons.[9]

Experimental

Chemicals and Apparatus.—The methyl phthalate used in these studies was obtained by fractionation of Eastman Kodak Co. white label grade through a total condensation, partial take-off type fractionating column, 2.5 × 90 cm., which was packed with 4 mm. glass helices. The middle portion boiling at 131–141° (3–6 mm.), was collected.

Methyl *o*-toluate was obtained by oxidizing *o*-xylene (Eastman Kodak, white label grade) to *o*-toluic acid (m. p. 104–105°) and converting this to the methyl ester. Fractional distillation gave a product boiling at 96–97° (15 mm.), $n^{25}\text{D}$ 1.5162.

The furnace employed had a heated core 60 cm. in length. Temperatures were recorded and controlled to ±5° by a Brown recording potentiometer, series 1100, *via* a chromel–alumel thermocouple longitudinally centered between the pyrolysis tube and the furnace core. The Sillimanite reaction tubes were 76 cm. long and had an internal diameter of 2.2 cm. Standard taper joints were cemented into the tube ends by means of asbestos, sodium silicate and Alundum cement to act as extenders and facilitate connection of traps, etc. Methyl phthalate was delivered to the top of the tube by means of a modified Cenco Gilson Pipetter.

The trapping system consisted of four glass traps connected in series and maintained at 20, 0, −78 and −78°, respectively. Following these were two ketene traps[10] containing water to collect any formaldehyde which had escaped the traps. A wet test meter to measure the gas volumes completed the train.[11]

Pyrolysis of Methyl Phthalate.—After the furnace attained constant temperature, the apparatus was swept with nitrogen. Then the nitrogen stream was discontinued and methyl phthalate was introduced at a constant rate until either a sufficient quantity had been pyrolyzed or until the tube became plugged. Gas samples were withdrawn at regular intervals and analyzed in a Burrell gas analysis apparatus, Model Tl A39-101.

After introduction of the ester was terminated, the traps were permitted to come to room temperature and the total volume of gas was recorded, as well as barometric pressure and the temperature of the wet test meter. The latter was taken as the temperature of the gas stream. The weight of condensed material was found by weighing the traps, removing the trapped material by washing with 200–300 ml. of anhydrous ether, and reweighing the empty traps. A small amount of this material was insoluble in ether. Its weight was added to that of the non-extractable material left in the traps and in the combustion tube to form the portion of products designated as carbon and tars.

The ether was then removed by fractional distillation through a total condensation, partial take-off column having a packed space measuring 0.5 by 90 cm. A continuous monel metal spiral served as the packing. At all temperatures except 1000° the distillate gave a positive Schiff test and paraformaldehyde[12] (m. p. 148–155°) sublimed into

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(9) Rittman, Byron and Egloff, *Ind. Eng. Chem.*, **7**, 1019 (1915).

(10) Bolstad and Dunbar, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 498 (1943).

(11) At 405° the small volume was measured by displacement of salt water from a Mariotte bottle.

(12) Formaldehyde was identified as the 2,4-dinitrophenylhydrazone, m. p. 165–166°.

the condenser. The amount of the latter was largest from the trials at 608°.

Quantitative analyses for that small part of formaldehyde which was collected in the water-filled ketene traps were performed on 150 ml. of distillate obtained by refluxing the trap contents with dilute sulfuric acid and distilling. The method described by Walker[13] was successful. However, application of this, or Denigès'[14] modified Schiff reagent, to the condensable portion of the pyrolysis products failed. Small amounts of polynuclear substances, particularly anthracene, were found to interfere.

After removal of the ether, residue (A) was weighed and moisture determinations were made by means of a Dean and Stark[15] apparatus. When no substance was present to form an azeotrope with water, a weighed amount of anhydrous reagent benzene was included in the mixture. Water was found among the products of pyrolysis only at 405°. Subsequent analyses for water in a known mixture gave an accuracy of only 47%.

The residue (B) left from the water determination, plus the water insoluble material which had distilled, was weighed and fractionally distilled through the spiral packed column. In this manner the amounts of benzene[16] (b. p. 77–80°), toluene[17] (b. p. 107–112°) and xylene (b. p. 134–146°)[18] were found. Continued distillation of a portion of residue (B) obtained from the products of pyrolysis at 608° permitted isolation of methyl benzoate[19] (b. p. 200°). However, attempts to distil methyl benzoate quantitatively were unsuccessful because of sublimation of the high molecular weight unsaponifiable materials.

The residue (C) left after the xylene determination was divided into three weighed portions. Part (C_1) was dissolved in dioxane and water and titrated with alkali. From this the number of grams of phthalic anhydride in (C) was calculated. Part (C_2) was saponified with standard alkali to determine the total number of equivalents of anhydride and esters.[20] Part (C_3) was saponified and the mixture was then extracted with benzene in a liquid-liquid extractor for twelve to eighteen hours. The benzene was distilled and the residual, unsaponified material (D) was dried in vacuum and weighed.

The saponification equivalent per gram of esters in (C) was now calculated from the results obtained by subtracting the sum of the weights of phthalic anhydride and the unsaponifiable material from the weight of (C), and the equivalents used to neutralize phthalic anhydride found in (C_1) from the total number of equivalents found in (C_2).

Determinations of the saponification equivalents of known mixtures of methyl benzoate and methyl phthalate had shown that these were linear functions of percentage composition, the experimental accuracy being 0.5–2.8%. Therefore, the composition of the ester portion of residue (C) was easily determined once the saponification equivalent per gram of ester in (C) was known.

In order to check the accuracy of these determinations a known mixture of the various components was analyzed according to the scheme just outlined. The figures in parentheses are, in order, grams present, % present, % found: carbon, as decolorizing charcoal (1.02, 0.46, 0.55); water (10.00, 4.53, 2.09), trioxane (2.04, 0.92, 0.00), benzene (43.44, 19.7, 17.2), toluene (8.51, 3.86, 3.86), *o*-xylene (6.54, 2.96, 3.19), phthalic anhydride (5.12, 2.32, 2.32), methyl benzoate (21.40, 9.70, 11.3), methyl phthalate (105.60, 47.9, 46.4), high molecular weight unsaponifiable[21] (16.95, 7.67, 7.59). The sum of the percentages found is 94.5.

Various attempts were made to identify the components of the unsaponifiable material (D). The material from one trial at 800° was separated into rough fractions by distillation under vacuum. Biphenyl[22] was found in one of these. Numerous recrystallizations from various solvents and several attempts to separate the components by adsorption failed to yield any identifiable, single substance.

Pyrolysis of Methyl *o*-Toluate.—Methyl *o*-toluate (120.7 g.) was pyrolyzed at 600°, the ester being introduced at the rate of 0.35 g./min. At the end of the pyrolysis no carbon remained in the reaction tube. The non-condensable products were not analyzed.

The condensable material (104.8 g.) was fractionally distilled through the spiral-packed column. Fraction I (b. p. 70–90°, 0.1 g.) was discarded. Fraction II (b. p. 105–110°, 4.2 g.) contained toluene, identified by conversion to 2,4-dinitrotoluene, m. p. 68–68.5°. Fraction III (b. p. 110–140°, 0.7 g.) was not examined. Fraction IV (b. p. 140–145°, 2.7 g.) contained *o*-xylene, identified as *o*-(2,3-dimethylbenzoyl)-tetrachlorobenzoic acid, m. p. 179–180°. Fraction V (145–195°, 0.3 g.) was discarded, but Fraction VI (b. p. 195–202°, 1.3 g.) consisted of methyl benzoate, identified by saponification to benzoic acid, m. p. 118–119.5°. Fraction VII (b. p. 202–208°, 0.8 g.) and VIII (b. p. 208–213°, 98.5 g.) contained methyl *o*-toluate.

In all, 32.0 g. (26.5%) of the methyl *o*-toluate decomposed to toluene (13.1%), xylene (8.5%), methyl benzoate (4.1%) and gases (50.0%).

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Summary

The pyrolysis of methyl phthalate has been studied at temperatures of 405, 608, 805 and 1000°. Degradation products have been identified and their amounts have been determined by analyses.

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[13] Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, p. 257.

[14] Walker, *ibid.*, p. 244.

[15] Dean and Stark, *J. Ind. Eng. Chem.*, **12**, 486 (1920).

[16] Identified as *m*-dinitrobenzene, m. p. 89°. When benzene had been added to the mixture, the refractive index of this fraction was used to check its purity.

[17] Identified as 2,4-dinitrotoluene, m. p. 68–69°.

[18] Identified as *o*-(2,3-dimethylbenzoyl)-tetrachlorobenzoic acid, m. p. 177–178°; *cf.* Underwood and Walsh, THIS JOURNAL, **57**, 941 (1935).

[19] Identified by saponification to benzoic acid, m. p. 121–122°, and conversion of the acid to benzanilide, m. p. 162–163°. Methanol was identified as methyl 3-nitrophthalate, m. p. 154–155°.

[20] The presence of methyl phthalate was shown by isolation of phthalic acid, m. p. 206–208° dec., and its conversion to phthalanil, m. p. 207°.

[21] Biphenyl, 5.08 g.; naphthalene, 7.73 g.; anthracene, 1.99 g.; and *p*-terphenyl, 2.15 g.

[22] Identified by melting point and mixed melting point, both 69–70°, and by conversion to 4,4'-dinitrobiphenyl, m. p. 234°.