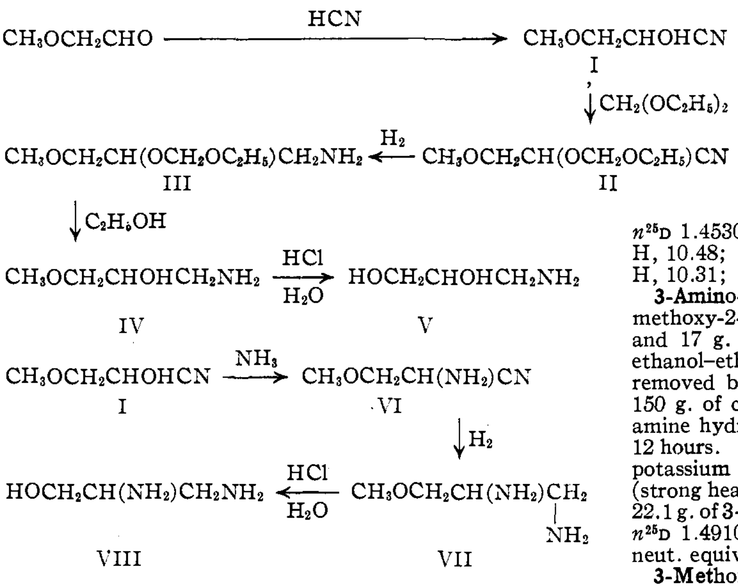

$$\mathrm{CH_3OCH_2CHO} \xrightarrow{\mathrm{HCN}} \underset{\mathrm{I}}{\mathrm{CH_3OCH_2CHOHCN}} \xrightarrow{\mathrm{CH_2(OC_2H_5)_2}} \underset{\mathrm{II}}{\mathrm{CH_3OCH_2CH(OCH_2OC_2H_5)CN}} \xrightarrow{\mathrm{H_2}} \underset{\mathrm{III}}{\mathrm{CH_3OCH_2CH(OCH_2OC_2H_5)CH_2NH_2}}$$

$$\underset{\mathrm{III}}{\mathrm{}} \xrightarrow{\mathrm{C_2H_5OH}} \underset{\mathrm{IV}}{\mathrm{CH_3OCH_2CHOHCH_2NH_2}} \xrightarrow[\mathrm{H_2O}]{\mathrm{HCl}} \underset{\mathrm{V}}{\mathrm{HOCH_2CHOHCH_2NH_2}}$$

$$\underset{\mathrm{I}}{\mathrm{CH_3OCH_2CHOHCN}} \xrightarrow{\mathrm{NH_3}} \underset{\mathrm{VI}}{\mathrm{CH_3OCH_2CH(NH_2)CN}} \xrightarrow{\mathrm{H_2}} \underset{\mathrm{VII}}{\mathrm{CH_3OCH_2CH(NH_2)CH_2NH_2}} \xrightarrow[\mathrm{H_2O}]{\mathrm{HCl}} \underset{\mathrm{VIII}}{\mathrm{HOCH_2CH(NH_2)CH_2NH_2}}$$

to room temperature and acidified with a few drops of H_3PO_4. Vacuum distillation gave 557 g. of 3-methoxy-2-hydroxypropionitrile, b.p. 86–90° (3–4 mm.), $n^{25}D$ 1.4240 (91% yield). Calcd. for $C_4H_7O_2N$: N, 13.85. Found: N, 13.89.

3-Methoxy-2-ethoxymethoxypropylamine.—3-Methoxy-2-hydroxypropionitrile (101 g.), 254 g. of ethylal, and 0.5 g. of H_2SO_4 were refluxed for one-half hour. The ethanol-ethylal azeotrope followed by excess ethylal was removed by distillation. Vacuum distillation of the residue gave 151.8 g. of 3-methoxy-2-ethoxymethoxypropionitrile, b.p. 86–87° (6 mm.), $n^{25}D$ 1.4140 (95% yield). Calcd. for $C_7H_{13}O_3N$: N, 8.79. Found: N, 8.98.

3-Methoxy-2-ethoxymethoxypropylamine.—A charge of 70.4 g. of 3-methoxy-2-ethoxymethoxypropionitrile, 102 g. of ammonia, and 30 g. of Raney nickel was hydrogenated at 108–125° and 450–700 atmospheres pressure in a stainless steel autoclave for one hour. A pressure drop of 400 atmospheres was noted. Vacuum distillation of the discharged product gave 65 g. of 3-methoxy-2-ethoxymethoxypropylamine, b.p. 68–71° (3 mm.), $n^{25}D$ 1.4280 (90% yield). Calcd. for $C_7H_{17}O_3N$: C, 51.53; H, 10.43; N, 8.59; neut. equiv., 163. Found: C, 51.37; H, 10.58; N, 8.38; neut. equiv., 160.

3-Methoxy-2-hydroxypropylamine.—A mixture of 45.1 g. of 3-methoxy-2-ethoxymethoxypropylamine, 150 g. of ethanol, and 22 g. of HCl (g) was refluxed for 15 minutes. The ethanol–ethylal azeotrope followed by excess ethanol was removed by distillation. The mixture was then neutralized with 60% potassium hydroxide. Vacuum distillation of the neutral solution gave 25.8 g. of 3-methoxy-2-hydroxypropylamine, b.p. 75–77° (2–3 mm.), $n^{25}D$ 1.4530 (88% yield). Calcd. for $C_4H_{11}O_2N$: C, 45.71; H, 10.48; N, 13.3; neut. equiv., 105. Found: C, 45.48; H, 10.31; N, 13.04; neut. equiv., 110.

3-Amino-1,2-propanediol.—A charge of 47.5 g. of 3-methoxy-2-ethoxymethoxypropylamine, 100 g. of ethanol, and 17 g. of HCl (g) was refluxed for 15 minutes. The ethanol–ethylal azeotrope followed by excess ethanol was removed by distillation. A solution of 75 g. of H_2O and 150 g. of concentrated hydrochloric acid was added to the amine hydrochloride and the resulting mixture refluxed for 12 hours. The mixture was cooled and neutralized with 60% potassium hydroxide. Vacuum distillation of the solution (strong heating necessary to drive out amine from salt) gave 22.1 g. of 3-amino-1,2-propanediol, b.p. 110–115° (1–2 mm.), $n^{25}D$ 1.4910 (yield 83%). Calcd. for $C_3H_9O_2N$: N, 15.38; neut. equiv., 91. Found: N, 14.94; neut. equiv., 91.5.

3-Methoxy-2-aminopropionitrile.—A charge of 119 g. of ammonia and 40 g. of 3-methoxy-2-hydroxypropionitrile was heated in a stainless steel autoclave at 48–65° for one hour. The discharged product was flashed distilled under vacuum and then redistilled under vacuum to give 15 g. of 3-methoxy-2-aminopropionitrile, b.p. 75–77° (1–2 mm.), $n^{25}D$ 1.4390 (yield 37%). Calcd. for $C_4H_8ON_2$: neut. equiv., 100. Found: neut. equiv., 99.9.

3-Methoxypropylenediamine.—A mixture of 10 g. of 3-methoxy-2-aminopropionitrile, 85 g. of ammonia and 30 g. of Raney nickel was hydrogenated at 100–152° and 325–700 atmospheres pressure for 1.5 hours. Vacuum distillation of the product gave 8.3 g. of 3-methoxy-1,2-propylenediamine, b.p. 46–48° (3–4 mm.), $n^{25}D$ 1.4505. Calcd. for $C_4H_{12}ON_2$: neut. equiv., 52. Found: neut. equiv., 56.

2,3-Diamino-1-propanol.—A charge of 13.5 g. of 3-methoxy-1,2-propylenediamine, 150 g. of concentrated hydrochloric acid and 100 g. of water was refluxed at 105–110° for 14 hours. The mixture was cooled and neutralized with 60% potassium hydroxide. The potassium chloride was filtered off and the filtrate vacuum distilled. A 50% yield of 2,3-diamino-1-propanol, 3.2 g., b.p. 108–110° (1–2 mm.), $n^{25}D$ 1.4935. Calcd. for $C_3H_{10}ON_2$: neut. equiv., 45. Found: neut. equiv., 47.5.

WILMINGTON, DELAWARE

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

The Pyrolysis of Phenyl Phthalate[1]

BY ROBERT P. ZELINSKI AND HARRY M. ANDERSEN[2]

The pyrolysis of phenyl phthalate at temperatures of 400, 600, 800 and 1000° has been studied. Qualitative and quantitative data concerning the products have been obtained, but a satisfactory degradation sequence has not been found.

As part of a study of the effect of temperature on the nature and amounts of the products obtained from the pyrolysis of some common plasticizers,[3] the pyrolysis of phenyl phthalate has been investigated. The literature appears to contain no report of the degradation of this ester although the pyrolysis of some alkyl phthalates has been studied.[3,4]

The experiments described in this investigation were carried out at temperatures of 400, 600, 800 and 1000° with the rate of introduction of phenyl phthalate at approximately 0.5 g./min. Sillimanite tubes were used as reaction chambers.

As expected, under comparative conditions phenyl phthalate was much less resistant to decomposition than methyl phthalate,[3] two-fifths

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(1) This work was performed with the aid of U. S. Navy funds under Subcontract 1, Contract 10431, a prime contract with the Hercules Powder Company, Allegheny Ballistics Laboratory.

(2) Taken in part from a thesis presented by Harry M. Andersen to the Graduate School of De Paul University in partial fulfillment of the requirements for the degree, Master of Science, 1950.

(3) R. P. Zelinski, J. T. Ziedlecki and A. L. Anderson, THIS JOURNAL, **72**, 5503 (1950).

(4) (a) N. Nagel and R. Abelsdorff, *Wiss. Veroffentlich Siemens-Konzern*, **5**, 193 (1926); *C. A.*, **21**, 1642 (1927); (b) H. Meyer and A. Hofmann, *Monatsh.*, **39**, 109 (1948).

being decomposed at 400° and over four-fifths at 600°. Essentially quantitative degradation took place at 800°.

Analysis of the condensable degradation products[5] obtained at 400° showed that they consisted of water (7.7%), free acid, as phthalic anhydride, (4.8%), phenol (12.9%), phenyl benzoate (72.8%) and a non-volatile, unsaponifiable fraction (2.0%). No carbonaceous material and only a negligible volume of gas were formed. At 600° the composition was water (7.8%), free acid (4.1%), phenol (14.0%), benzene (1.9%), phenyl benzoate (33.7%) and an unsaponifiable fraction (17.4%). Increasing the temperature to 800 or 1000° did not alter the nature of the identifiable products although it had a considerable effect on the quantities of each. The amount of carbonaceous material rapidly increased as the temperature was raised until at 1000° about half of the decomposed ester appeared in this form. These and other data are more completely given in Table I.

TABLE I

PYROLYSIS OF PHENYL PHTHALATE

Temp., °C.	400	600	800	1000
Charge, g.	129.2	118.1	127.0	52.3
Rate, g./min.	0.54	0.50	0.53	0.64
Recovery, g.	128.1	117.0	122.6	51.1
Ester decomp.				
Grams	52.0	104.3	124.1	52.3
%	40.6	88.3	98.5	100.0
Products, g.				
Carbon and tars	0.0	7.8	21.7	23.3
Water	4.0	8.1	7.7	2.2
Phthalic anhydride	2.5	4.3	1.0	0.1
Unsaponifiable[a]	1.0	18.1	32.9	2.9
Phenol	6.7	14.6	6.3	1.6
Benzene	0.0	2.0	11.9	4.8
Phenyl benzoate	37.9	35.1	10.1	2.9
Gases	0.0	14.3	32.4	14.5
Gases, l. at S.T.P.	0.0	8.55	25.9	19.6
Gases, vol. %				
Carbon dioxide		42.6	26.9	11.4
Carbon monoxide		56.7	57.4	37.4
Hydrogen		0.7	15.3	50.6
Acetylene		0.0	0.2	0.6

[a] Exclusive of benzene, phenol and water.

The non-condensable products from the pyrolyses were relatively simple mixtures of carbon dioxide, carbon monoxide and hydrogen, with a minor quantity of acetylene as the only other component. At 600° the gas consisted almost entirely of the two carbon oxides; but as the reaction temperature was raised, the volume percentage of hydrogen rapidly rose, mainly at the expense of carbon dioxide, until at 1000° half the gas volume was hydrogen.

Biphenyl was isolated as the principal component (*ca.* 50%) from the unsaponifiable, neutral fraction obtained at 600°. A high-boiling liquid, possibly phenyl ether, comprised the major portion of this fraction at 800°. Efforts to prepare picric salts of these neutral fractions were uniformly unsuccessful, indicating the probable absence of any considerable amount of polynuclear hydrocarbons. This is in accord with the observation[6,7] that polynuclear hydrocarbons are only minor products of the pyrolysis of benzene unless alkylbenzenes or olefins are also present.

After considering the analytical data we are at present unable to formulate equations which might express the sequences of degradation. This is particularly true for the experiments at 400° where decomposition had proceeded to a satisfactory extent, but with the absence of carbonaceous matter and all but a negligible amount of gas. The major reaction is the conversion of phenyl phthalate to phenyl benzoate, but the conversion yield is distinctly better than 100% on a mole basis, implying a degradation to phenyl benzoate and a partial recombination of the fragmented residue to form more phenyl benzoate. Thus at 400° there was obtained 0.19 mole of phenyl benzoate from the 0.16 mole of phenyl phthalate which was decomposed.

Experimental

Chemicals and Apparatus.—The phenyl phthalate used in these studies melted at 71–73° and had a saponification equivalent of 161 (theoretical, 159).

The electrically heated furnace was constructed in the University machine shop and had a heated length of 60 cm. It was mounted vertically. Temperature was recorded and controlled to ±3° by means of a Brown recording potentiometer, series 1100, activated by a chromel–alumel thermocouple located between the wall of the furnace core and the wall of the pyrolysis tube.

The pyrolysis tubes were Sillimanite and had an internal diameter of 2.2 cm. Standard taper, glass joints were cemented into the tube ends to facilitate attachment of the traps and the charging device. Introduction of solid phenyl phthalate at a slow and constant rate was accomplished by a device described elsewhere.[8]

The trapping system, and gas sampling, measuring and analysis apparatus, were substantially the same as those described earlier[3] except that the ketene traps were omitted.

Pyrolysis Procedure.—After the furnace attained constant temperature, the complete pyrolysis train, including the ester-delivering apparatus, was swept with nitrogen. In the experiments at 400 and 600° the nitrogen stream was discontinued during pyrolysis, but at higher temperatures it was necessary to maintain the nitrogen flow to prevent plugging. The flow was metered and adjusted so that the effluent gas was about 25% nitrogen. Gas analyses were made at regular intervals.

When introduction of phenyl phthalate was terminated, the volume of gas, barometric pressure and the temperature of the wet test meter (assumed to be the temperature of the effluent gas), were recorded.

The traps, tared beforehand, and combustion tube were weighed, and the contents were extracted several times with commercial Carbitol, the last time with hot solvent. The Carbitol solution was then further diluted to exactly 1000 ml. Traps and combustion tube were further extracted with water, dried and reweighed. It was then possible to calculate the weight of the condensable product which was soluble in Carbitol, and the weight which was insoluble and reported as part of carbon and tars. The combustion tube was treated in a similar fashion and then burned clean in a stream of air and oxygen. Reweighing and calculation gave an additional quantity of carbon and tars. The last part of this quantity was obtained by diluting an aliquot of the

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(5) Parenthesized values are percentages by weight of the phenyl phthalate decomposed.

(6) For a bibliography, see C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1929, pp. 93–108.

(7) L. Hurdon and E. Reid, THIS JOURNAL, **50**, 3066 (1928).

(8) H. Andersen and R. P. Zelinski, *Anal. Chem.*, **22**, 1461 (1950).

Carbitol solution, which contained a fine suspension of carbon, with twice its volume of acetone, filtering, drying the precipitate, and weighing.

Analytical Procedure.—In the gas the only hydrocarbon found to be present was a small concentration of acetylene.

The portion of products designated as carbon and tars was not analyzed.

All analyses for the components of the condensable portion were performed at least in duplicate on aliquots of the Carbitol solution. The accuracy of the methods was examined by adding known amounts of the component being determined to other aliquots and by analyzing these. Substantially all of the added components were found by these analyses.

Water was determined by titration with toluene of a solution of a 10.0-ml. aliquot in 10.0 ml. of Carbitol to an arbitrary but reproducible cloud point. The volume so needed was corrected by means of a blank run on 20.0 ml. of Carbitol. The amount of water present was then found by comparison to an experimentally determined graph relating weight of water in 20.0 ml. of Carbitol to volume of toluene. This was practically a linear relationship over the range from 10 to 200 mg. of water. The accuracy of the method was checked by combining samples of two different and separately analyzed solutions of water in Carbitol and determining the amount of water present. The sum of weights of water found by separate analyses was 176 mg.; the weight found by analyzing the combined solution was 180.

Benzene was determined by distillation of a 50.0-ml. aliquot through a Todd fractionating column.[9] All material boiling up to 80° was collected as benzene and no evidence of any simple benzene homolog was ever found when distillation was continued. Qualitative identification of benzene was effected by converting part of the distillate to *m*-dinitrobenzene, m.p. 89–91°. The precision of the method was tested by addition of a weighed amount of benzene to an aliquot, followed by distillation. Some 94–99% of the added benzene was recovered.

The weight of phenol present was found by bromination[10] to 2,4,6-tribromophenol. A 10.0-ml. aliquot, diluted with 500 ml. of distilled water, was employed. Addition of measured amounts of phenol (*ca.* 10–20% of that found) to such an aliquot, followed by analysis, indicated that 99.3% of the added phenol was found. Furthermore, experiments showed that neither benzene, phenyl phthalate nor biphenyl interfered in the analysis. The presence of phenolic compounds other than phenol is possible, but it is believed that they constitute no more than 5% of the quantity designated as phenol.

The presence of small amounts of other phenolic compounds was indicated by bromination of the phenol portion obtained from the saponification of an aliquot of the Carbitol solution. The basic saponification mixture was extracted with benzene, acidified, and made alkaline with sodium bicarbonate. Extraction with ether removed the phenolic fraction which, after evaporation of the ether, was treated with bromine water. The resultant precipitate consisted of tribromophenol and a small quantity of dark brown material which was separated. The tribromophenol showed no mixed melting point depression with an authentic sample. Recrystallization of the dark brown portion gave a substance melting at 95–96°.

Acidification of the bicarbonate solution described above gave a mixture of acids which was separated by extraction with chloroform, evaporation of the chloroform, and steam distillation. Benzoic acid, m.p. 121°, was recovered from the distillate and converted to *p*-bromophenacyl benzoate, m.p. 113–115° (lit. m.p. 119°). Ether extraction of the residue left by removal of benzoic acid, followed by evaporation and steam distillation, gave phthalic acid, m.p. 201–204°, which was converted to phthalanil, m.p. 207–210°. These two acids comprise the major portion of the free or esterified carboxylic acids present. This was shown by saponification of an aliquot of the Carbitol solution, titration with sulfuric acid to determine the equivalents of acids and esters present, acidification with more sulfuric acid, and steam distillation. Titration of the distillate accounted for 87% of the equivalents, presumably the steam-volatile benzoic and phthalic acids and phenol.

Free acid, calculated as phthalic anhydride, was determined from the number of equivalents of alkali needed to titrate a 25.0-ml. aliquot, diluted with 500 ml. of water, to the phenolphthalein end-point.

The weight of the non-volatile, unsaponifiable portion was found by saponification of a 50.0-ml. aliquot followed by a three-hour extraction of the alkaline solution with benzene in a liquid–liquid extractor. The benzene solution was washed with ten 50-ml. portions of water to remove Carbitol and then distilled to remove two-thirds of the benzene. The remaining benzene was removed by evaporation in a stream of dry air, and the residue was dried to constant weight *in vacuo*. Weighed amounts of typical unsaponifiable compounds, when added to the original aliquot, could be measured with a precision of 97 to 102% by this procedure.

The total number of equivalents of free acid and esters was obtained by saponification of a 25.0-ml. aliquot with standard alkali. By correcting for the equivalents of free acid and for the weight of unsaponifiable material present, it was possible to obtain the true saponification equivalent of the condensable pyrolysis products. Finally, since the saponification equivalents of known mixtures of phenyl benzoate and phenyl phthalate are linear functions of percentage composition, the composition of the ester portion of the degradation products could be computed.

The non-volatile, unsaponifiable portions could not be purified by recrystallization and failed to form a picrate. The liquid–solid mixture obtained from pyrolysis at 600° was sublimed at 80° (4 mm.) four times to give a 50% yield of biphenyl, m.p. and mixed m.p. 62–66° (lit. 70°), which was brominated to 4,4′-dibromobiphenyl, m.p. 165–168°.[11] Part of the liquid unsaponifiable portion was separated by decantation and distilled. A fraction boiling at 250–260° was collected but could not be converted to a picrate. A considerable portion boiled above 300°.

CHICAGO 14, ILLINOIS RECEIVED APRIL 16, 1951

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[9] Manufactured by the Todd Scientific Glass Apparatus Company, Drexel Hill, Pa. The Nichrome spiral packing was used.

[10] F. Treadwell and W. Hall, "Analytical Chemistry," 9th Eng. ed., Vol. II, John Wiley and Sons, New York, N. Y., 1942, p. 633.

[11] R. Scholl and W. Neovius, *Ber.*, **44**, 1087, Note 1 (1911).