[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITITE OF TECHNOLOGY]

Rates of Distillation of the Benzene Carboxylic Acids and Their Methyl Esters

BY GEORGE SCHULZ[1] AND H. C. HOWARD

In studies of methods for separation and identification of the acids in the complex mixture resulting from controlled oxidation of bituminous coal, it was desirable to have information as to the rates of distillation of authentic samples of acids of the benzene carboxylic series and of their methyl esters. For determining absolute rates of evaporation, complicated apparatus is required, which is tedious and inconvenient to operate. However, it is possible to obtain useful approximations with a very simple type of molecular still, such as is used in the present work.

Experimental

Apparatus.—For determining the rates of distillation the apparatus shown in Fig. 1 was employed. This was connected through the standard taper joint to a large bore stopcock and this in turn to the vacuum pumps. A small side arm with a capillary tip, and located between the joint and the stopcock, was sealed off at the beginning of an experiment and broken at the close to permit bringing the still quickly to atmospheric pressure. The first experiments were carried out with the mechanical pump alone; the latter ones with a diffusion pump backed by the mechanical pump. A McLeod gage sealed on between the still and the stopcock showed pressures of approximately 10^{-1} mm. with the mechanical pump, and less than 10^{-3} mm. with the diffusion pump backed by the mechanical pump. In most of the experiments heat was applied to the still by an electrically heated cast aluminum block, the temperature of which was controlled by insertion of a small vapor pressure type controller, filled with a liquid of appropriate vapor pressure for control in the temperature range desired. The temperature of the aluminum block was read from a certified Bureau of Standards thermometer and varied ±2° from the desired temperature. Temperature variations inside the still itself were no doubt much less. In one experiment with hexamethyl mellitate, in which more precise temperature control was desired, heating was effected by a well agitated oil-bath in which the temperature variation was ±0.5°. The absolute temperature of the evaporating surface was not known, but was, of course, lower than that of the constant temperature bath. The condenser of the still was cooled by a mixture of Dry Ice and ethylene trichloride.

Materials.—The sources of the acids and methods of purification, when used, were as follows: *o*, *m* and *p*-phthalic, trimesic, pyromellitic and benzenepentacarboxylic acids (Eastman Kodak Company). The phthalic, trimesic and pyromellitic acids were used without purification. The trimellitic, hemimellitic, prehnitic and mellophanic acids were prepared by Dr. Lee I. Smith and were used without purification. The Eastman benzenepentacarboxylic acid was purified as follows: A solution of the sodium salt was decomposed by electrolysis in a three-compartment cell. The free acid from the anode compartment was recrystallized from nitric acid and gave an equivalent weight of 60.1, theoretical 59.63. The mellitic acid was prepared in this Laboratory by oxidation of carbon black and purified by precipitation as the ammonium salt and recovery of the free acid by electrolysis. The equivalent weight was 57.2, theoretical 57.0. Methyl esters were prepared by reaction with diazomethane. The esters were purified by crystallization from methanol or methanol-water mixtures. All the methyl esters were white, crystalline compounds with melting points within the range reported in the literature, except those of *o*-phthalic and trimellitic acids which were liquids. The dimethyl and dibutyl phthalates were Eastman products and were used without further purification.

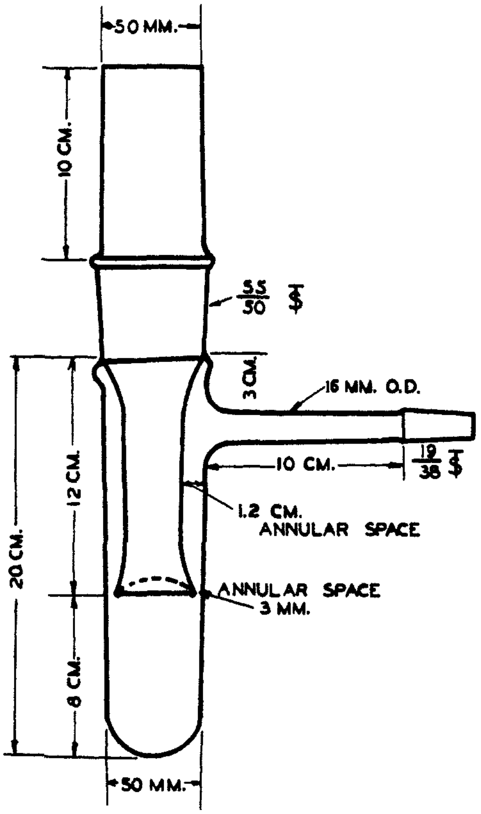

Fig. 1.—Molecular still.

Procedure.—For determining the rates of distillation an approximately 1-g. sample, accurately weighed, was introduced into the still in a tared, flat bottom glass container, 3.2 cm. in internal diameter and 5 cm. deep. The superficial evaporating area was 8 sq. cm., but the actual area of the surface from which evaporation took place was unknown. After a preliminary evacuation at room temperature the aluminum block or oil-bath, which had previously been brought to the desired temperature, was placed in position and raised until it was just under the sidearm of the still and the distillation carried out for the required time. At the conclusion of the experiment the still was cooled rapidly and the glass tip broken to bring the system to atmospheric pressure. The still was then disconnected at the ground joint and the excess refrigerant poured out of the condenser. The large ground joint connecting condenser and still was then warmed by running tap water over it and the condenser and adhering layer of distillate quickly removed. The greater part of the condensate layer was found on the bottom of the condenser and extended only a few mm. up the sides even in those experiments where the mechanical pump alone was employed and in which the pressures were too high for straight path distillation. The distillate was washed off the condenser with an appropriate solvent, water or acetone, into small

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tared beakers, the solvent evaporated on a water-bath and the residue weighed.

Results and Discussion

Rates of evaporation in vacuum are given by the Langmuir equation:[2] $w = p \times s \times k\sqrt{M/T}$, where w is the rate; p, the vapor pressure; s, the surface area; M, the molecular weight and T, the absolute temperature. For any given substance at constant temperature and for constant evaporating areas, the rate is determined by the vapor pressure, p. If the temperature is varied one would expect a nearly linear relation between log w and $1/T$, since there is an exponential relation between p and T, and considerable changes in T produce only small changes in $\sqrt{1/T}$. Within the limits of error of the experimental method used this has been found to be the case for the methyl esters of the benzene carboxylic acids.

Preliminary experiments with the free acids showed that even the highest member of the series, mellitic, could be distilled unchanged if heated rapidly to about 310°. However, attempts to determine rates of distillation of the isomeric phthalic acids, using low heating rates, led to irregular results except in the case of the *o*-isomer. With the *o*-phthalic acid the expected increment in rate with increasing temperature was realized, but with the other isomers the rates of distillation were irregular and those at higher temperatures appeared to depend upon how long the sample had been heated previously at some lower temperature. It is probable that this behavior is due to the formation of polymeric anhydrides[3] by the *m*- and *p*-isomers. Such compounds would have lower vapor pressures than the monomeric acids. In the case of the *o*-isomer this effect would not appear since the anhydride is monomeric.

The data on the rates of distillation of the free acids were difficult to reproduce and the positions of the polar groups were found to affect very markedly the rates of distillation of isomers. With the tricarboxylic acids, hemimellitic (1, 2, 3) showed a distillation rate approximately 100-fold that of trimesic (1, 3, 5) at 150° and at 200° there was a thousand-fold difference.[4]

In view of the probable disturbing effects of anhydride formation in fractionating a mixture of free acids, attention was turned to the methyl esters. Conversion of the carboxyl groups to esters resulted in elimination of differences of rates among isomers, within the experimental accuracy of our procedure, with the possible exception of tetramethyl pyromellitate which, in the experiments at 10^{-1} mm. pressure, showed rates of distillation significantly higher than the esters of the isomeric tetracarboxylic acids. It is evident that the fractionation obtained by distillation of the mixed esters will be largely on the basis of molecular weight.

All the methyl esters of the benzenecarboxylic acids proved to be perfectly stable under these distillation conditions. The same sample of hexamethyl mellitate was repeatedly distilled without decomposition as shown by absence of non-volatile residue, failure to discolor, constant melting point and constant rate of distillation.

Representative data are illustrated by Fig. 2. Two curves are shown for the rates of distillation of hexamethyl mellitate, one at about 10^{-1} mm. and the other at 10^{-3} mm. The other curves show the rates of distillation at 10^{-3} mm. of the esters of the lower members of the series. The hexamethyl mellitate at the lower pressure distills at a significant rate at temperatures as low as 150°. There is no evidence from these curves of any significant change in rates of distillation below and above the melting point.

The constants in the equations for the rate data, calculated by least squares, are given in Table I.

TABLE I

RATES OF DISTILLATION OF METHYL ESTERS

Log $w = a + b/T$; rates in mg./hr.

	a	b
Mellitic	17.58	−6318
Pentacarboxylic	18.01	−6272
Pyromellitic	18.11	−5955
Trimellitic	14.70	−4059
o-Phthalic	12.32	−2885

The activation energies of the distillation process, which approximate the heats of vaporization, calculated from the slopes, range from 13,000 cal. for *o*-dimethyl phthalate to 29,000 cal. for the hexamethyl mellitate.

For purposes of comparison rate measurements were also made on dibutyl phthalate. The rate of distillation of dibutyl phthalate in the apparatus described was found to be almost identical with that of trimethyl trimellitate. Vapor pressure–temperature relations for dibutyl phthalate have been reported by two sets of workers,[5] and the values, calculated for 55° in mm. of mercury, are 8.8 and 9.4 × 10^{-4}, respectively. The value for 55° calculated from the present data on rates of distillation at bath temperatures of 34 and 75° is 1.4 × 10^{-4}. In the calculation of vapor pressure by the Langmuir equation the following assumptions are implicit: that the true evaporating area is given by the superficial area, that all the molecules leaving the evaporating surface are condensed without collision or re-evaporation and that the temperature of the evaporating surface is that of the constant temperature bath in which the still is immersed. None of these requirements is strictly fulfilled in any molecular dis-

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[2] Jones, Langmuir and Mackey, *Phys. Rev.*, **30**, 201 (1927).

[3] Bucher and Slade, THIS JOURNAL, **31**, 1319 (1909).

[4] Very great differences in the volatility of the isomers of hydroxybenzoic acid have been reported by Sidgwick, *J. Chem. Soc.*, **117**, 396 (1920).

[5] Hickman, Hecker and Embree, *Ind. Eng. Chem., Anal. Ed.*, **9**, 264 (1937); Verhoek and Marshall, THIS JOURNAL, **61**, 2737 (1939).

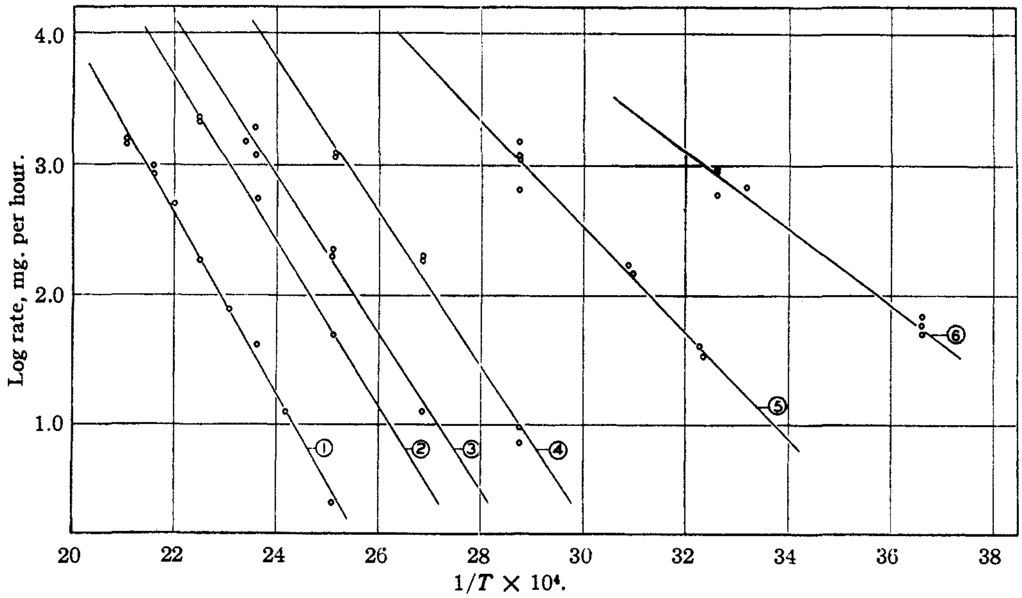

Fig. 2.—Rates of distillation of methyl esters: 1, 2—mellitate; 3—pentacarboxylate; 4—pyromellitate; 5—trimellitate; 6—o-phthalate.

tillation and they were, of course, not met in the simple experimental method described. Of these factors, increase of evaporating area by "creeping" of the liquid film would give high results; collisions between molecules and between molecules and walls as well as imperfect condensation, low results, and evaporating surface temperatures lower than those recorded by the bath also will give low results. An evaporating surface temperature lower than that of the bath is inevitable, both because of the gradient through the walls of the still and the heat losses to the condenser. Assuming the correctness of the vapor pressure data in the literature, it is evident that absolute rates of distillation found in this small still for any given bath temperature are too low by a factor of approximately six. The data have, however, been of great value in studies of the separation of complex mixtures of esters of acids of the benzene carboxylic series.

Examination of the curves of Fig. 2 shows very great differences in rates of distillation of the esters of various members of the series. For example, at 25° dimethyl phthalate distills

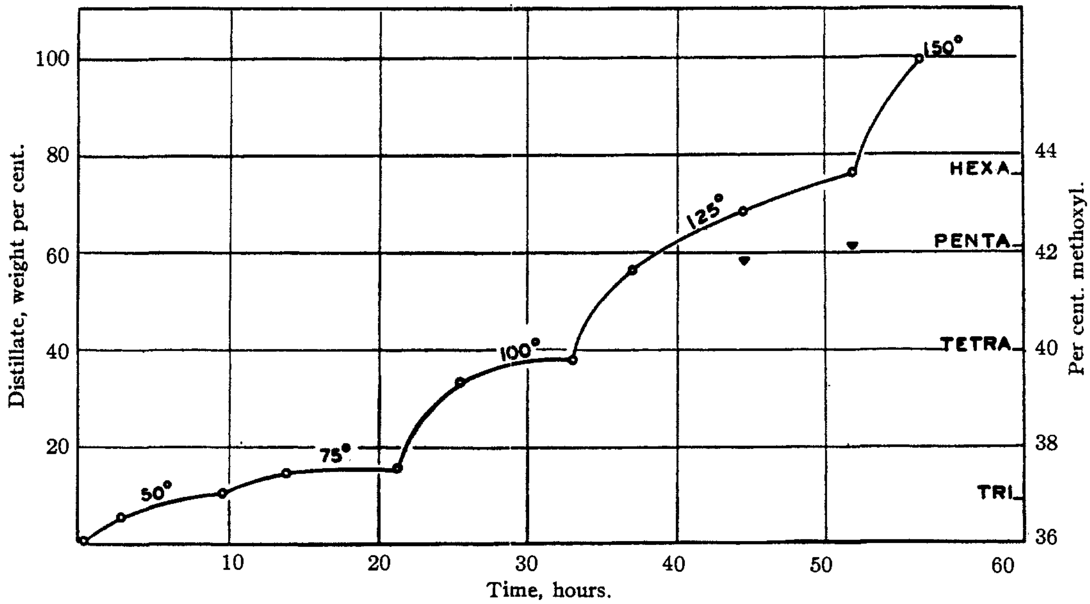

Fig. 3.—Distillation of mixture of authentic esters.

approximately 40 times as rapidly as trimethyl trimellitate and, hence, the distillate from an equi-molecular mixture will be much richer in the more volatile component.

In Fig. 3 are shown plots of an exhaustive stepwise distillation of an approximately equi-molecular mix of the neutral methyl esters of *o*-phthalic, trimellitic, pyromellitic, benzene pentacarboxylic and mellitic acids. The solid line shows the cumulative per cent. distillate as a function of time and the triangles the methoxyl content of the fractions. It is evident that by such a procedure a rough fractionation is effected and that by the application of this process to an unknown mixture of methyl esters of the benzene carboxylic series information can be obtained, on even small samples, of the relative amounts of the various members of the series present. The application of this method of examination to the mixture of esters of the acids obtained by alkaline permanganate oxidation of bituminous coal will be described elsewhere.

Summary

Rates of distillation in vacuum of the methyl esters of *o*-phthalic, trimesic, trimellitic, hemimellitic, prehnitic, mellophanic, pyromellitic, benzene pentacarboxylic and mellitic acids have been measured. Plots of the log of the rate against the reciprocal of the absolute temperature are linear. The slopes of these lines lead to values of heats of vaporization ranging from 13 kcal. for dimethyl *o*-phthalate to 29 kcal. for hexamethyl mellitate. No significant difference was found in the rates of distillation of the methyl esters of isomeric acids except with the tetracarboxylic acids where there was evidence that the pyromellitic is the most volatile. The rate of distillation of trimethyl trimellitate was found to be of the same order as that of dibutyl phthalate over the range 35–75°. The applicability of the molecular still to fractionation of the methyl esters of the organic acids formed by oxidation of bituminous coals has been pointed out.

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Oxidation Products of Certain Petrographic Constituents of Bituminous Coals

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The chemical reactions of the petrographic constituents of coal have been studied by a number of investigators and in some instances wide differences in rate of oxidation or of hydrogenolysis[2] have been reported. An obvious objection to the use of rate measurements as a criterion of chemical difference lies in the great effect that purely physical factors such as surface, porosity and state of molecular aggregation may have on over-all rates of reaction. In this work an attempt has been made to determine, by isolation of degradation products of established structure, what fundamental chemical differences may exist between certain of the petrographic constituents.[3] The method applied consisted of strong oxidative degradation to water soluble acids followed by recovery and esterification of the acids and fractionation of the esters.[4]

Since it is not possible to obtain pure samples of the petrographic constituents, the work was carried out on samples which represented as high a concentration of the particular constituent concerned as it was practical to obtain. The petrographic description and chemical composition of the samples studied are given in Table I. The Pittsburgh Seam coal is predominantly "bright," over 90% anthraxylon and translucent attritus[5]; the sample from the High Splint coal was hand-picked to furnish a high content of opaque attritus, estimated[6] to be 60%; the fusain was hand-picked from the Illinois No. 6 bed[7] and the product from the Utah coal[8] had been separated by flotation and presumably consisted largely of "resins." There are striking differences between these materials in ultimate composition. The atomic carbon–hydrogen ratios range from over 2 for the fusain sample to 0.7 for the resins. The high C/H for fusain points to a large content of highly condensed cyclic structures. A single aromatic ring surrounded symmetrically by three others has a C/H of 1.5; with six surrounding rings the ratio rises to 2.0 and increases slowly as additional peripheral rings are added. The low C/H for the resins shows the presence of considerable hydroaromatic or aliphatic structure; three aliphatic carbon atoms

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(1) Present address: Neville Company, Neville Island, Pittsburgh, Pennsylvania.

(2) Fuchs, Gauger, Hsiao and Wright, *Mineral Industries Penna. State Coll.*, **23** (1938); Yohe and Harman, *Trans. Illinois State Acad. Sci.*, **32**, No. 2, 134 (1939). For a general discussion of effect of type of coal on hydrogenolysis see Lowry, "Chemistry of Coal Utilization," John Wiley and Sons, New York, N. Y., 1945, p. 1757.

(3) Bone and Bard, *Proc. Roy. Soc.* (London), **162A**, 495 (1937), have applied alkaline permanganate oxidation to certain petrographic constituents of three British coals. No significant differences between oxidation products were found, but a very much lower rate of oxidation of fusain was reported.

(4) For methods of oxidation see Juettner, THIS JOURNAL, **59**, 208, 1472 (1937). For methods of esterification and fractionation of the esters see Schulz and Howard, THIS JOURNAL, **68**, 991 (1946).

(5) Fieldner, *et al.*, *U. S. Bur. Mines, Tech. Paper*, **525** (1932).

(6) This was a part of Bureau of Mines sample B3, see *Ind. Eng. Chem.*, **31**, 1160 (1939).

(7) From St. Ellen Mine.

(8) From Hiawatha Mine, Hiawatha, Utah.