[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

Purification and Freezing Point of Phenanthrene[1]

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A method for the large-scale purification of commercial phenanthrene is described. After the removal of anthracene by maleic anhydride, fluorene and carbazole are completely removed by azeotropic distillation with diethylene glycol at suitable reduced pressures. The effect of these various tricyclic compounds on the freezing point of phenanthrene was determined. Pure phenanthrene has a freezing point of 99.15° and a cryoscopic constant of 11.65°/mole solute/1000 g.

As usually isolated from coal tar, phenanthrene contains minor quantities of fluorene, anthracene and carbazole. These impurities are difficult to remove, and thus very pure phenanthrene has been unavailable commercially. As part of a long-range program, looking toward the isolation and purification of polynuclear aromatic compounds that may occur in the oils produced by coal hydrogenation processes, the possibility has been examined of securing pure phenanthrene by methods amenable to large scale processing. In the petroleum industry, the use of azeotropic distillation is extensively employed for the purification of hydrocarbons and the attractive possibilities of this technique led us to consider its applicability to the polynuclear field. Examination of various entrainers of the polyglycol type, boiling in the desired range, showed that diethylene glycol is effective as a selective entrainer for phenanthrene.

The study of the effect of pressure on the distillate compositions of diethylene glycol solutions of phenanthrene and of the three tricyclic fused-ring compounds that occur with it in coal tar, showed that both phenanthrene and anthracene form azeotropes with diethylene glycol, the hydrocarbon content of which decreases as the pressure is increased. Carbazole does not form an azeotrope. At all pressures, fluorene apparently forms azeotropes; these all possess high concentrations of hydrocarbon, and have boiling points lower than those of pure fluorene and considerably lower than those of the phenanthrene azeotrope.

The chemical separation of anthracene from phenanthrene can be achieved by any of several known methods, such as the formation of an adduct with maleic anhydride,[2] dimerization by ultraviolet light,[3] or oxidation by various agents.[4,5] Perhaps the most convenient method is adduct formation with maleic anhydride (see Experimental).

On the basis of the above facts, a separation scheme was evolved for the large-scale purification of commercial phenanthrene. Anthracene is removed first by reaction with maleic anhydride. The residual product is then distilled with excess diethylene glycol in a column operating at 5 to 10 plates at a pressure of 200–300 mm. Under these conditions, all the fluorene is removed in the azeotrope. The pressure is then decreased to 20 mm. and the distillation continued until all the phenanthrene is distilled. The residue contains carbazole. The polynuclear substances are recovered by dilution of the glycol solution with water. By following this procedure, about 75% of the original phenanthrene is recovered as phenanthrene of at least 98 mole per cent. purity.

The azeotrope of phenanthrene and diethylene glycol contains only about 4% of hydrocarbon, and thus the distillation of large quantities of material is required when much phenanthrene is desired. The dilute solution has the advantage, however, of being liquid at room temperature, and the various problems associated with the distillation of solid materials are avoided.

The freezing point of pure phenanthrene is 99.15°. Its cryoscopic constant is 11.65 degrees per mole in 1000 g. of phenanthrene. This compares with the value of 12 in the literature,[6] and 11.0[7] calculated from the heat of fusion of 4.45 kcal./mole. The cryoscopic constant is of interest in the determination of the average molecular weight of solubilized coal, as phenanthrene has been shown to be an excellent solvent for bituminous coal.[8]

Experimental

Preparation of Pure Compounds. a. Chemical Purification of Phenanthrene.—A sample of commercial phenanthrene was found to have the following composition[9]: phenanthrene, 80.4%; anthracene, 9.4%; carbazole, 3.8%; fluorene, 2.0%; other impurities, 2.0%. The impure phenanthrene was separated from the bulk of the anthracene by refluxing 671 g. with 184 g. of maleic anhydride in 1250 ml. of xylene under nitrogen for 22 hours. The mixture was filtered, the filtrate extracted with sodium hydroxide solution, and the organic layer freed from solvent by distillation. The residue was stirred under nitrogen for two hours with 7 g. of sodium.[10] It was then vacuum distilled and yielded 511 g. of product. Two recrystallizations from 30% benzene in alcohol gave 289 g. of phenanthrene. Analysis of this product by ultraviolet spectrophotometry[11] indicated the presence of 0.065% anthracene. As shown below, this sample still contained some fluorene and carbazole. The freezing point of this material, as determined by the time-temperature method, using a platinum resistance thermometer,[12] was 98.963 ± 0.006°.

b. Anthracene.—A sample of commercial anthracene was purified by distillation with ethylene glycol according to the method of Yule.[13] Two crystallizations from benzene solution gave material with a freezing point of 216.042 ± 0.003° as measured by a cooling curve and 216.041 ± 0.003° as measured by a warming curve.

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[1] Presented before the Organic Division of the American Chemical Society at Chicago, Illinois, September 3, 1950.

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[3] N. S. Capper and J. K. Marsh, *J. Chem. Soc.*, 724 (1926).

[4] F. L. Cohen and U. Cormier, THIS JOURNAL, **52**, 4363 (1930).

[5] W. E. Bachmann, *ibid.*, **57**, 555 (1935).

[6] F. Garelli and A. Ferrantini, *Atti. acad. Lincei*, [5] **2**, I, 275 (1893).

[7] P. W. Robertson, *J. Chem. Soc.*, **81**, 1233 (1902).

[8] C. Golumbic, J. E. Anderson, M. Orchin and H. H. Storch, Bureau of Mines Report of Investigations 4662 (1950).

[9] Determined by Drs. C. Golumbic and R. A. Friedel by a combination of chromatography, countercurrent distribution and ultraviolet spectrophotometry.

[10] G. Schroeter, *Ber.*, **57**, 2025 (1924).

[11] G. Bradley and J. K. Marsh, *J. Chem. Soc.*, 650 (1933). We wish to thank Dr. R. A. Friedel for the quantitative determination of the anthracene content of the phenanthrene samples.

[12] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 335 (1945).

[13] J. A. C. Yule, U. S. Patent 2,213,755 (1938).

c. **Fluorene.**—A middle cut of 415 g., b.p. 160° (15 mm.), was obtained from the distillation of 504 g. of Kopper's best grade of fluorene. This was twice recrystallized from benzene-alcohol solution to yield a product having a melting point of 114.8–115°.

TABLE I

EFFECT OF ADDITION OF IMPURITIES ON FREEZING POINT OF PHENANTHRENE

Compound	ΔT/mole per cent. impurity, °C.
Anthracene	+0.625[a]
Fluorene	−0.092[a]
2,2'-Dimethyldicyclopentyl	−0.660
Dodecane	−0.660
Carbazole	+1.70[a]

[a] Solid solutions.

TABLE II

AZEOTROPES OF PHENANTHRENE AND ANTHRACENE WITH DIETHYLENE GLYCOL

	Phenanthrene		Anthracene	
Pressure, mm.	B.p., °C.	Concn., mole per cent. hydrocarbon	B.p., °C.	Concn., mole per cent. hydrocarbon
20	146	4.34	147	0.8[a]
50	166	3.62	166.5	.8[a]
100	180	2.30	184	.8[a]
150	196	1.49	196	.8[a]
200	203	1.02	200	.8
300	217	0.33	217.5	.4
400	226	.10	226	.1

[a] Anthracene insoluble at these concentrations.

TABLE III

AZEOTROPIC DISTILLATION OF PHENANTHRENE WITH DIETHYLENE GLYCOL

		Distillation		Hydrocarbon content						
Fraction number	Volume in ml.	Pressure in mm.	Temperature, °C.	Weight	Weight per cent. of original	Cumulative weight per cent.	Per cent. of fraction	Freezing point, °C.	Anthracene content mole per cent.	Mole per cent. purity of phenanthrene[a]
1, 2	7.1	260	88	0.45	0.08	0.08	6.3	.....	..	...
3	51	260	207	4.5	.82	.90	8.8	.....	..	...
4, 5	78	260	211	4.0	.73	1.63	5.1	......	..	...
6–8	212.6	100	173	12.8	2.34	3.97	6.0	.....	..	...
9–11	382.7	100	178	18.7	3.42	7.39	4.9	.....	..	...
12–16	244.2	20	143	26	4.75	12.14	10.6	97.673	0.99	95.76
18, 19, 21, 23, 25	49.1	20	143	4.0	.73	12.87	8.15	.....	.87	...
17, 20, 22, 24	626	20	144	48	8.77	21.64	7.67	98.700	.85	97 79
26–32	927	20	145	73	13.35	34.99	7.88	98.995	.81	98.15
33–39	1180	20	147	87	15.90	50.89	7.37	99.126	.85	98.45
40–57	2286	20	145	161	29.45	80.34	7.04	99.459	.86	99.01
58–65	975	20	145	50	9.14	89.48	5.13	99.253	.83	98.59
66–71	881	20	145	32	5.86	95.34	3.63	99.061	.70	98.56
72–75	793	20	147	14	2.56	97.90	1.76	.....	.66	...
Residue	147	20	...	11.5	2.10	100.00	7.8	245	..	00.0[b]
Total	8840			547						

[a] Fluorene and carbazole absent, and assuming all other impurities do not form solid solutions. [b] Carbazole.

d. **Carbazole.**—A solution of 64 g. of 90–93% carbazole, m.p. 226–233°, was dissolved in approximately 300 ml. of concentrated sulfuric acid. The dark colored solution was extracted with three 200-ml. portions of benzene and then stirred into 1600 ml. of an ice–water mixture. The resulting flocculent, tan-colored precipitate was filtered and washed with a little water. The dried material was recrystallized once from benzene and once from pyridine–benzene solution and gave 7.6 g. of crystals, m.p. 240–243°.

e. **Diethylene Glycol.**—Diethylene glycol was purified by fractionation in a 4-ft. long, 1-in. diameter heli-grid column at 100 mm. pressure, b.p. 182°, n^{25}_{D} 1.4460.

Change in Freezing Point with Impurities.—The apparatus used to determine the freezing point of the solid sample was essentially that described for use with liquid hydrocarbons,[12] but with some modifications for regulating the bath temperature. The sample tube was immersed to about $^{3}/_{4}$ of its length in silicone oil contained in a one-gallon dewar flask. The oil in the flask was stirred and was either rapidly heated by a variable 500 watt immersion heater, or cooled by a copper coil containing circulating water. The temperature was maintained constant to about 0.5° by means of a "Thermocap" relay system actuated by a sliding clip on a thermometer in the bath.

Increments of about 0.3 mole per cent. of impurity were added to purified phenanthrene and the freezing points were determined up to 2% impurity content. The freezing points varied linearly with the mole per cent. impurity, indicating the absence of association effects at the concentrations tested. The results are shown in Table I.

Study of Azeotropic Composition.—A 3-ft. long, 22 mm.-diameter heli-grid column was used in these experiments. The properties of the binary systems were studied by refluxing in this column, solutions containing 20 g. of the polynuclear compound in 200 ml. of the entrainer. Several milliliters of impurities were removed, and then 1-ml. samples of distillate were taken every half-hour at a 60:1 reflux ratio. The composition of the distillate was determined by comparison of its refractive index with a calibration curve made from known mixtures. The results for the binary systems of diethylene glycol with phenanthrene and with anthracene appear in Table II. Fluorene distilled over as a solid at all pressures, while carbazole did not appear at all in the distillate.

Preparation and Freezing Point of Synthetic Phenanthrene.—A large sample of phenanthrene was prepared by a slightly modified version of the procedure of Bachmann and Struve.[14] This method consisted of the succinoylation of naphthalene followed by Clemmensen reduction of the mixture of keto acids. The γ-naphthylbutyric acids were cyclized by the method of Wilds,[15] and the resulting tetrahydrophenanthrene was dehydrogenated with 30% palladium-on-charcoal by refluxing for four hours. The over-all yield in the five-step synthesis was 20%. The ultraviolet spectrum of this synthetic phenanthrene indicated that it contained 0.75% anthracene which obviously originated from the cyclization of some of the γ-(2-naphthyl)-butyric acid into the 3-position of naphthalene. Since about half of the mixture of γ-naphthylbutyric acids was the 2-isomer,[16] at least 1.5% of the 2-isomer closed into the 3-position of the naphthalene nucleus. The freezing point of the synthetic

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[14] W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 472 (1939).

[15] A. L. Wilds, THIS JOURNAL, **64**, 1421 (1942).

[16] L. F. Fieser and M. Peters, *ibid.*, **54**, 4347 (1932).

TABLE IV

PROPERTIES OF VARIOUS SAMPLES OF PHENANTHRENE

Sample	Description of sample	Known impurities (wt. per cent.) Anthracene	Carbazole	Fluorene	Freezing point, °C. Observed	Corrected for known impurities
1	Commercial, as received	9.4	3.8	2.0	100.85	(88.7)
2	Commercial, treated with maleic anhydride and sodium and twice recrystallized	0.065	0.3	Present	98.963	98.01
3	Sample 2 distilled azeotropically and twice recrystallized	.093	.00	0.00	99.177	99.113
4	Commercial, treated with maleic anhydride and distilled azeotropically	.86	.00	.00	99.459	98.909
5	Synthetic	.75	.00	.00	99.621	99.152

phenanthrene containing 0.75% anthracene was 99.621°. When corrected for the anthracene content, the freezing point was 99.152°, compared with 99.113° found for phenanthrene purified by azeotropic distillation. Recrystallization of the synthetic phenanthrene from ethanol increased the anthracene content to 1.06% (ultraviolet spectrometry) and also raised the freezing point to 99.812°. As the increase of 0.31% of anthracene, indicated by ultraviolet spectrometry, should increase the freezing point by 0.31 × 0.625 = 0.194°, and as an actual increase of 0.191° was observed, the cryoscopic and ultraviolet data are self-consistent.

Purification of Phenanthrene by Azeotropic Distillation. A. Chemically Purified Phenanthrene.—The sample of phenanthrene which had been purified by chemical methods was distilled with excess diethylene glycol in a 4-ft. long, 1-in. diameter heli-grid column, first at 100 mm., then at 20 mm. pressure. The distillate fractions were mixed with four to five times their volumes of water to precipitate the hydrocarbons which were filtered by suction and washed well with water. The aqueous filtrate was concentrated by evaporation on a steam-bath and then vacuum distilled to recover the glycol. The small quantity of solid (impure fluorene?) recovered from the first fraction had a melting point of 89–92°. Dilution of the residue with water precipitated the carbazole which, after crystallization from aqueous alcohol, melted at 242–245°. The middle third of the distillate, containing the bulk of the phenanthrene, was precipitated, filtered, washed, and recrystallized twice from alcohol to remove occluded glycol. In the final crystallizations, the phenanthrene was centrifuged and washed with ice-cold alcohol. The freezing point of this material was 99.141 ± 0.003°. Further crystallization from alcohol resulted in increasing the freezing point to 99.179 ± 0.003° as determined by cooling and warming curves. Ultraviolet analysis showed the presence of 0.093% anthracene. The exact purity could not be estimated because of the possibility of the presence of undetected impurities which form solid solutions. It appeared, however, that the sample was very pure since it froze sharply over an extremely narrow temperature range. When impurities are present, the range is much greater, whether solid solutions are formed or not, and it becomes more difficult to determine freezing points by warming curves.

B. Commercial Phenanthrene.—In the preferred procedure, a 580-g. sample of commercial (80%) phenanthrene was refluxed with 165 g. of maleic anhydride in xylene solution, the mixture filtered, the filtrate extracted with alkali, and the xylene evaporated. The residue of 558 g. was distilled with excess diethylene glycol from a 5-liter flask through a 3-ft. long, 1-in. diameter heli-grid column. The fractions were precipitated by dilution with water, the separated solids were centrifuged, washed well with water, and dried at 65°. Some of the fractions were dissolved in a small quantity of acetone and reprecipitated with water, others were crystallized from alcohol. The fractions and their properties are listed in Table III.

The best sample of phenanthrene, obtained from this distillation, had a freezing point of 99.459° and contained 0.86% anthracene. The properties of the various samples of phenanthrene described in these experiments appear in Table IV.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization Accompanying Alkylation. VII.[1] Reaction of Benzene with Methylcyclopropane, Ethylcyclopropane and with Dimethylcyclopropanes

BY HERMAN PINES, WILLIAM D. HUNTSMAN[2a,2b] AND V. N. IPATIEFF

The alkylation of benzene with methyl-, dimethyl- and ethylcyclopropanes was studied. Methylcyclopropane reacted with benzene in the presence of hydrogen fluoride to give pure *s*-butylbenzene. Ethylcyclopropane reacted with benzene in the presence of hydrogen fluoride, sulfuric acid and aluminum chloride. The monoalkylated product consisted in each case of about 63% of 2- and 37% of 3-phenylpentane. 1,1-Dimethylcyclopropane with benzene in the presence of hydrogen fluoride formed *t*-amylbenzene, while 1,2-dimethylcyclopropane gave *t*-amylbenzene and smaller amounts of 2- and 3-phenylpentane, and 2-phenyl-3-methylbutane. The infrared spectra of six of the amylbenzenes are reported.

The alkylation of benzene with compounds containing a cyclopropane ring has received relatively little study. The only examples reported in the literature are those in which cyclopropane itself was used as the alkylating agent. In the presence of hydrogen fluoride,[3] aluminum chloride[4] or sulfuric acid[5] catalysts at low temperatures (0–35°) the sole monoalkylated product isolated was *n*-propylbenzene. With a sulfuric acid catalyst at 65°, the monoalkylated product consisted of isopropylbenzene.[4a]

The complete absence of isopropylbenzene in the

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[1] For paper VI of this series, see H. Pines, J. D. LaZerte and V. N. Ipatieff, THIS JOURNAL, **72**, 2850 (1950).

[2] (a) Universal Oil Products Predoctoral Fellow, 1947–1950. (b) Abstracted from the dissertation submitted to the Department of Chemistry, Northwestern University, in partial fulfillment of requirements for the degree of Doctor of Philosophy in August, 1950. Presented in part before the Organic Division, American Chemical Society, Chicago, Ill., September, 1950.

[3] J. H. Simons, S. Archer and E. Adams, THIS JOURNAL, **60**, 2955 (1930).

[4] (a) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940); (b) A. V. Grosse and V. N. Ipatieff, *ibid.*, **2**, 447 (1947).

[5] V. N. Ipatieff, H. Pines and B. B. Corson, THIS JOURNAL, **60**, 577 (1938).