[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Nitrogen Compounds in Petroleum Distillates. IX. Nitrogen Bases from California Cracked Gasoline[1]

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The crude bases for this investigation, 242 cc., b. p. 115-240°,[2] were extracted from four barrels of pressure distillate, b. p. 36–171°, obtained in cracking *gas-oil*, from Los Angeles Basin petroleum, and *crude residuum* from San Joaquin Valley petroleum, at 454° and 54–58 atmospheres.

Nine bases, consisting of quinoline, quinaldine, and seven pyridine homologs, were isolated and there is no reason to suspect that any base, present beyond negligible amount, was overlooked. *Non-aromatic* types, which are present along with *aromatic* types in *straight-run* kero bases in a percentage ratio of approximately 85:15, respectively,[3] were not encountered among the *cracked* gasoline bases which obviously are pyrolysis products of more complex molecules, including aromatic and non-aromatic bases together with inert nitrogen compounds.[4] At the temperature of the cracking plant non-aromatic bases are evidently unstable and, it may be, undergo dehydrogenation and molecular rearrangement to more stable aromatic types. Whereas both quinoline and quinaldine occur in cracked gasoline, a careful search carried out in the Texas Laboratory has not revealed either of these products or any monoalkyl quinoline in straight-run distillates. Since a number of polymethylated quinolines have been identified in straight-run distillates, dealkylation may be assumed as at least one effect produced at high temperatures on aromatic bases and it is equally certain that, through pyrolytic degradation of polynuclear aromatics, there arise at times pyridine or its homologs.

Due to the limited supply (130 cc.) of bases available, it was impractical to fractionate this small volume exhaustively through an effective column by the usual procedure. To circumvent this difficulty, resort was had to the indirect micro method, termed Amplified Distillation,[5] which originated with the authors.

An inspection of Table I reveals that, because of the proximity of boiling points (144–145.3°, 157–158°, 170.3–171.6°) within three pairs of the gasoline bases, it was impractical to separate individual products, free of admixtures, through fractional distillation alone.

Experimental

Action of *p*-Toluenesulfonyl Chloride on the Bases.—The crude material (154.5 cc. or 139.3 g.) was added to 851 cc. of 3 *N* sodium hydroxide and 272 g. of *p*-toluenesulfonyl chloride was stirred in over a period of forty-five minutes with the temperature at 25–30°. A temperature of 60–70° was then maintained for fifteen minutes, after which the cooled solution (A) was extracted with several 200-cc. portions of ether (B), followed by withdrawal of the bases (112 cc.) from the latter with four 200-cc. portions of 1 *N* hydrochloric acid. Since there was no precipitation of sulfonamides on strong acidification of the ethered out solution (A), it was evaporated to dryness, 400 cc. of concentrated hydrochloric acid was added and the mixture was refluxed for thirty hours. After removal of the excess acid in steam, caustic soda was added and the free bases (18 cc.) were distilled out with steam. These bases proved to be exclusively tertiary and accordingly were combined with the 112 cc. of unchanged bases recovered from the toluenesulfonyl chloride treatment. The residue from evaporation of the ether solution (B) on being processed like solution (A) yielded no bases. From these results it is evident that the Hinsberg separation of amines is unreliable when applied to a complex mixture of petroleum bases.

Amplified Distillation.—To the 130 cc. of bases was added 2438 cc. of acid- and caustic-washed hydrocarbon oil boiling evenly over a 90–240° range. This mixture was distilled at a 10:1 reflux ratio through a 1 × 105-cm. spirally-indented, adiabatic column, cuts being made in 1° fractions (D). A second fractionation from a smaller still-pot was performed as follows: the still was charged with the lowest fraction, 1D, which was then topped in 1° cuts to the minimum temperature of 2D, when this second fraction was added. The procedure was repeated in ascending order of boiling points until all the D fractions were distilled. Finally a third distillation was carried out in like manner on the fractions from the second distillation. The final 1° cuts from multiple distillation boiled over a 35–260° range, with the bases segregated between 98–236°, *i. e.*, in 139 fractions, each with an average base content of around 1 cc.

The base-hydrocarbon fractions were agitated over three-minute periods with three successive 0.5–0.7 volumes of 4 *N* hydrochloric acid, followed by 0.5 volume of water. In order to withdraw *non-aromatic hydrochlorides* each of the acid extracts was agitated for thirty minutes with an equal volume of chloroform.[3] A very small amount of

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(2) This material was assembled by the Union Oil Company of California.

(3) T. S. Perrin and J. R. Bailey, THIS JOURNAL, **55**, 4136 (1933).

(4) *Cf.* E. J. Poth, *et al.*, *ibid.*, **52**, 1240 (1930).

(5) Bratton, Felsing and Bailey, *Ind. Eng. Chem.*, **28**, 424 (1936).

TABLE I

BASES FROM PRESSURE DISTILLATE

Product	B. p.,[9] °C.	$n^{25}D$[9]	Isolated as	M. p. crude salt, °C.	Salt no.	Wt. of salt, mg.	Source of fractions	M. p. pure salt, °C. Eguchi[7]	Beilstein[8]	This work
2-MP[a]	129.3	1.4983	Picrate	164–165	1	782	98–118	165	164, 165	165.5
2,6-DMP	144	1.4953	Picrate	162–163	2	181	128–135	162	161	163
4-MP	145.3	1.5029	Picrate	162–165	3	617	119–129	167	167	167
2,5-DMP	157	1.4982	$HgCl_2$ salt	201–203	4	621	142–150	197[9]	162–164	168.5–169.5
			picrate					167	151–152 156–157 165.5	
2,4-DMP	158	1.4984	Picrate	181–183	5	139	137–140	182	179	182.5–183
			$HgCl_2$ salt	130–131	6	2688	142–156	131–132	132	131.5–132
			picrate	172–173.5	7	50	Bases from picrates E[b] 158–173			
2,4,6-TMP	170.3	1.4959	$HgCl_2$ salt	154–155	11	2784	155–167		154	
			picrate	154–155	12	420	Bases from picrates E 163–173	157	155–156 155–156	155.5–156
3,5-DMP	171.6	1.5032	$HgCl_2$ salt	253–259	8	496	142–167			
			$HgCl_2$ salt	168–169	9	384	155–162		170	
			picrate	242.5–243.5	10	20	Bases from picrates E 168–173	244	172–173 228–230	245
Quinoline	238.1[10]	1.6245[8]	Picrate	202–204	13	1270	199–220		203	203–203.5
2-MQ	247.6[10]	1.6093[8]	Picrate	190–193	14	125	225–233		191	193–194

[a] MP = Methylpyridine; DMP = Dimethylpyridine; TMP = Trimethylpyridine; MQ = Methylquinoline.
[b] See below, "Treatment of Unresolved Bases."

bases recovered from the combined chloroform extracts proved to be *aromatic*. From this result, *the occurrence of non-aromatic bases in cracked gasoline, regardless of its source, is not to be expected;* in any event, so far as concerns the processing of the bases under investigation, chloroform extraction of their hydrochlorides was superfluous.

In order to remove chloroform, the separate acid fractions were steamed out and the bases were freed with caustic and distilled in steam. Sulfur dioxide was then run into the separate distillates to methyl orange acidity, excess picric acid solution was added and precipitation was allowed to proceed under thermostatic control over four-hour periods at 50, 35° and finally at the minimum temperature allowable without separation of picric acid.

Water saturated with sulfur dioxide will not precipitate picric acid from its aqueous solution saturated at the same temperature; so temperature-solubility curves of picric acid in water[6] made possible a regulation of the minimum temperature at which picration could be effected with avoidance of any separation of picric acid.

Where picrates were not freed of admixtures through recrystallization, they were converted to mercuric chloride salts and an exchange in the two types of salts was repeated as often as necessary for final purification. The confusion which often arises from the formation of different mercuric chloride salts of an individual base was eliminated by observance of specific conditions which led to definite products, usually of the formula Base·$HCl \cdot 2HgCl_2$. For conversion of a picrate to a mercuric chloride salt, the base was liberated, steam distilled and titrated to slight acidity (methyl orange) with 0.506 *N* hydrochloric acid. Through the use of a mercuric chloride solution saturated at 25°[6] (p. 409) it was possible to carry out precipitation with exactly 2 moles of mercuric chloride per mole of base-hydrochloride. Minimum allowable cooling curves were again used as controls in fractional precipitation of the salts over a maximum temperature range. Where a salt appeared with a mercury content greater than in the formula Base·$HCl \cdot 2HgCl_2$, an adjustment was made in the amount of the reagent, such as to ensure complete precipitation of the bases.

Table I summarizes the properties of the salts obtained from the amplified distillation fractions. In recombination of individual salts from various fractions, prior to their purification and identification, it is obvious from the wide overlap of the origin of the corresponding bases, that the salts were combined from broader bands of distillation fractions than might seem warranted.

Treatment of Unresolved Bases.—In order to rework the regained residual bases from the salts described above, they were dissolved in 1 liter of sulfurous acid solution, excess picric acid (15 liters) was added and the bases were liberated from both the precipitated (D) and dissolved (E) picrates. This material gave the following constants.

	Cc.	G.	B. p., °C.	$n^{25}D$	Sp. gr. 28.5/25.6
Bases from D	29	26.6	116–225	1.5002	0.9172
Bases from E	27.5	25.1	116–200	1.4953	.9157

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(6) Seidell, "Solubilities of Inorganic and Organic Compounds," 2d ed., D. Van Nostrand Co., New York, 1919, p. 492.

(7) Eguchi, *Bull. Chem. Soc. Japan*, **2**, 176 (1927); **3**, 227, 235 (1928); *Chem. Zentr.*, **98**, 1223 (1927); **100**, 331 (1929).

(8) Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. XX, 1935.

(9) Errera, *Ber.*, **34**, 3700 (1901).

(10) Michael, *Ber.*, **18**, 2020 (1885).

The bases from E, *without admixture with hydrocarbon oil*, were fractionated in the usual way into 5° cuts through a 1 × 105-cm. column with a 10:1 reflux ratio. Crystalline salts were obtained from all of the first seven fractions boiling up to 164°; the remainder yielded only smears. Final purification through an exchange in salt types was effected as follows: mercuric chloride salts ⟶ picrates ⟶ mercuric chloride salts ⟶ picrates. The products isolated and identified as picrates were 2,4-dimethylpyridine, 3,5-dimethylpyridine and 2,4,6-trimethylpyridine; in other words, the presence of only three of the nine bases (Table I) identified through amplified distillation could be confirmed. This comparison establishes beyond question the superiority of amplified distillation over straight distillation in the resolution of complex mixtures of petroleum bases.

The bases from (D) were processed similarly to those from (E) but no pure individual product was isolated.

Purification and Identification of Salts

Each of the salts listed below was synthesized for a comparison of the two samples by solubilities, crystalline form and mixed melting points.

2-Methylpyridine.—Picrate 1 was recrystallized from water in long (2 cm.) spear-like clusters of slender prisms melting at 165.5°.

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: N, 17.39. Found: N, 17.51.

4-Methylpyridine.—Picrate 3 was recrystallized from water in clusters of flat feather-like needles (1.5 cm.) melting at 167°.

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: N, 17.39. Found: N, 17.55.

2,6-Dimethylpyridine.—Picrate 2 was recrystallized from water in microscopic prisms melting at 163°.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.45.

2,5-Dimethylpyridine.—The mercuric chloride salt 4 was converted to the picrate which crystallized from water in long (2 cm.) spear-shaped clusters of thin prisms melting at 168.5–169.5°. The synthetic picrate prepared by the method of Errera[9] (p. 3691) melted at 167.5–168.5° (Errera reported 165.5°).

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.43.

2,4-Dimethylpyridine.—Picrate 5 from water formed slender prisms melting at 182.5–183° in agreement with the synthetic product, m. p. 182.5°.[10] The picrate is far less easily purified than is the mercuric chloride salt.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.49.

3,5-Dimethylpyridine.—Picrate 10 separated from water in single slender needles (5 mm.) melting at 245°.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.91.

2,4,6-Trimethylpyridine.—Picrate 12 crystallized from water in short interlacing needles melting at 155.5–156°.

Anal. Calcd. for $C_{14}H_{14}O_7N_4$: N, 16.00. Found: N, 16.12.

Quinoline.—Picrate 13 crystallized from 50% alcohol in very short needles melting at 203–203.5°.

Anal. Calcd. for $C_{15}H_{10}O_7N_4$: N, 15.64. Found: N, 15.65.

Quinaldine.—The melting point of picrate 14 after several recrystallizations from acetone rose from 191–192° (reported in the literature) to 193–194°. This solvent is to be preferred to water or alcohol. Nitrogen determination on the lower melting sample ran 0.3–0.5% below the calculated per cent.

Anal. Calcd. for $C_{16}H_{12}O_7N_4$: N, 15.05. Found: N, 14.98.

Summary

Seven pyridine homologs, quinoline and quinaldine were isolated through *amplified distillation* of 130 cc. of California pressure distillate gasoline bases. In contrast to *straight run* distillates in the same temperature range, which contain in preponderant amount *non-aromatic* bases, only *aromatic* bases were encountered in the *cracked* gasoline.

The present investigation offers conclusive proof of the efficiency of amplified distillation as an indirect micro method in exhaustively fractionating small volumes of complex mixtures of petroleum bases.

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