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

The Nitrogen Compounds in Petroleum Distillates.[1] IV. Cumulative Extraction[2] of Kero Bases.[3] The Isolation of 2,4,8-Trimethylquinoline among the Kero Bases

BY T. S. PERRIN AND J. R. BAILEY

Introduction.—The kero bases represent a very complex mixture of both aromatic and non-aromatic types in a percentage ratio of approximately 15:85, respectively. Especially as concerns the non-aromatic bases, the direct isolation of pure products from distillation fractions can be attained through fractional crystallization of their salts only in exceptional cases.

It is obvious that a practical method of separation of the bases into aromatics and non-aromatics, would simplify the isolation of individual products. Based on the observation of a wide difference in the distribution ratio of salts of the two families between water and certain solvents immiscible with water, a process, which accomplishes this end in a most satisfactory way, has been perfected and found of general application over the entire range of kero bases.

The present investigation has disclosed a ready solubility of the hydrochlorides of the non-aromatic bases in chloroform, as compared with a lesser solubility of the aromatic hydrochlorides, and among the latter are included the hydrochlorides of both pyridine and quinoline homologs. Furthermore, the non-aromatic hydrochlorides are very soluble in water, whereas corresponding salts of some of the methylated quinolines encountered crystallize nicely from water.

In resolution of petroleum bases into the two types, the following procedure will be found serviceable, where either crude bases or distillation fractions are employed. The bases are dissolved in an excess of 1:1 hydrochloric acid and the solution extracted with an equal volume of chloroform. Instead of chloroform, ethylene chloride may be used and, on account of the much lower cost, it should prove serviceable in industrial extraction. The initial chloroform extraction effects a high concentration of the aromatic hydrochlorides in the aqueous layer and of the non-aro-

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(1) The investigation of organic nitrogen bases from the crude kerosene distillate of California petroleum was originally undertaken in connection with American Petroleum Institute Project 20, entitled: "Isolation and Investigation of Nitrogen Compounds Present in Petroleum."

For this research the Union Oil Company of California furnished the material, consisting of bases which were assembled when the refinery was operating largely on McKittrick crude from the San Joaquin Valley field and having a nitrogen content of 0.64%. Only recently the Texas Laboratory received three barrels of bases obtained from 3000 barrels of Edeleanu kerosene extract. This sulfur dioxide extract represents 25% of the kerosene fraction and the latter 5% of the crude oil refined; so it is evident that 80,000 barrels of California petroleum yield approximately 1 barrel of kero bases. However, all the crude distillates contain bases; so their aggregate amount would be considerably larger, were the gasoline, gas oil and lubricating oil fractions included.

(2) "Cumulative extraction" is explained in the text.

(3) "Kero bases" is an abbreviation for "kerosene bases."

matic hydrochlorides in the chloroform layer. In further segregation, the water layer is extracted several times with chloroform and the chloroform layer several times with water. Since there is always an appreciable difference in the refraction of the two types of bases within any boiling point range, refractive index determinations offer a convenient control at every stage of the process.

Its extensive application seems to warrant a specific name for this process and "Cumulative Extraction" is proposed, as embodying in a concise way the general result attained in progressive concentration of the aromatic hydrochlorides in water and the non-aromatic hydrochlorides in chloroform.

Cumulative extraction has been of especial service in simplifying isolations already accomplished by other methods, and in extending this work. Previous papers of this series have reported the isolation of 2,3,8-trimethylquinoline,[4] b. p. 280°, and of a naphthenic base of the formula $C_{16}H_{25}N$, b. p. 278.2°.[5] By the distribution of the salts of the fraction containing these two bases between water and chloroform, the separation and purification has been simplified greatly, and a third substance, 2,4,8-trimethylquinoline, has been isolated from the same distillation fraction (275° zone). The new procedure has been of further use in separation of 2,3- and 2,4-dimethylquinoline from the fractions in the 265° zone, and it is superior to an alternate method, described in Paper V of this series and which makes use of sulfur dioxide. Paper VI records the isolation, by cumulative extraction, of 2,8-dimethylquinoline from the 253° fraction of bases.

In final separation of the aromatics from small amounts of non-aromatics, either the free bases or their hydrochlorides can be converted in acetone solution to sulfates. The aromatic sulfates in great part separate from the solvent in crystalline form and the non-aromatic sulfates remain dissolved. It is evident also that both types of hydrochlorides can be converted directly to picrates, as well as mercuric chloride and zinc chloride double salts; however, corresponding salts of non-aromatic bases separate from mixtures almost invariably as non-crystallizing smears. It will be found advisable in picrating hydrochlorides to buffer the solution with sodium acetate; otherwise, where an excess of picric acid is used, it precipitates along with the picrates.

The employment of cumulative extraction has revealed the presence of aromatics and non-aromatics in all distillation fractions of kero bases. The boiling points and refractivities of several products, encountered below the quinoline range, indicate pyridine homologs. Where an aromatic base of known boiling point is suspected, it will be found, if present, in maximum concentration in a fraction boiling 3 to 5° lower than its own boiling point and, even when present in very small amount, it can be

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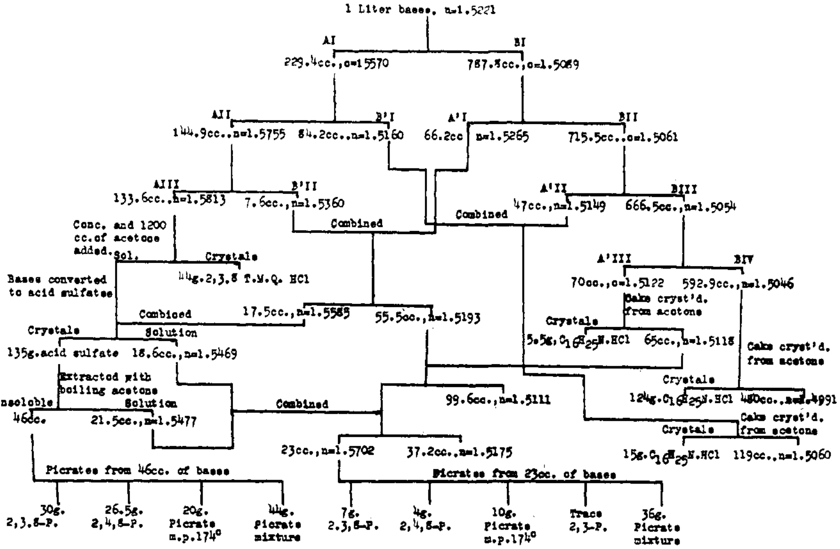
[4] W. A. King and J. R. Bailey, THIS JOURNAL, **52**, 1245 (1930).

[5] W. C. Thompson and J. R. Bailey, *ibid.*, **53**, 1002 (1931).

segregated from accompanying non-aromatics until its isolation in pure form is greatly simplified. A search for the common coal-tar bases, quinoline, isoquinoline, quinaldine and lepidine has given only negative results.

Experimental Part

Cumulative Extraction of a Distillation Fraction of Kero Bases Boiling at 273° and with n_D^{27} 1.5221.—One liter of bases[6] in one liter of 1:1 hydrochloric acid was extracted with 1200 cc. of chloroform and the aqueous layer AI separated from the chloroform layer BI. AI was washed with 400 cc. of chloroform, yielding fractions AII and B'I, followed by extraction of AII with 250 cc. of chloroform to yield fractions AIII and B'II. In a similar way BI was extracted with three successive portions of water, 400, 400 and 1000 cc., being split finally into fractions A'I, A'II, A'III and BIV. The accompanying flow-sheet is self-explanatory.



Flow-sheet in cumulative extraction.

"A" refers to hydrochlorides in water. "B" refers to hydrochlorides in $CHCl_3$. "n" = "n_D^{27}." "Cake" refers to residue after removal of solvent. "2,3,8-P" and "2,4,8-P" = "Picrates of 2,3,8- and 2,4,8-trimethylquinoline," respectively. "2,3-P" = "2,3-Dimethylquinoline picrate." Volumes, where given, refer to free bases.

The volumes of bases were arrived at by measuring the oil liberated with caustic soda from a fractional part of the hydrochloride solutions. The samples, after being dried, were used for refractivity determinations and finally converted to hydrochlorides before recombination with the fractions from which they were taken. A list of the end-products from processing the one liter of bases follows: 44 g. of 2,3,8-trimethylquinoline hydrochloride; 37 g. of 2,3,8-trimethylquinoline picrate; 30.5 g. of 2,4,8-trimethylquinoline picrate; 30 g. of unknown picrate, m. p. 174°; 80 g. of mixture of low melting picrates; 144.5 g. of hydrochloride of the $C_{16}H_{25}N$ base; 735.8 g. of non-aromatic bases (4 fractions, n_D^{27} 1.4991 to 1.5175).

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(6) This material was purposely not exhaustively fractionated.

Isolation of 2,4,8-Trimethylquinoline.—This product was encountered by King and Bailey[7] at the time 2,3,8-trimethylquinoline was discovered, but was not identified.

After concentration of the aromatic bases by cumulative extraction of the 273° fraction, the ready solubility of 2,4,8-trimethylquinoline hydrochloride in water and of its

TABLE I

EVALUATION OF THE AROMATIC AND NON-AROMATIC CONTENT OF DISTILLATION FRACTIONS OF KERO BASES

	B. p. and refr. of original samples		Admixed hydrocarbon oil		Vol. and refr. of bases in water layer		Vol. and refr. of bases in $CHCl_3$ layer		
No. of distil.	B. p., °C.	n^{27}_D	Vol., cc.	n^{27}_D	Vol., cc.	n^{27}_D	Vol., cc.	n^{27}_D	Bases in water layer, %
IV	182	1.4816	2.1	1.4600	3.2	1.4918	4.7	1.4860	40.6
III	193	1.4898	0.8	1.4910	3.9	1.4930	5.3	1.4851	42.4
IV	196	1.4888	.5	1.4687	4.1	1.4912	5.4	1.4832	43.2
V	200	1.4888	.4	1.4851	3.9	1.4951	5.7	1.4857	40.6
IV	205	1.5006	Naphthalene cryst.	1.5878	2.1	1.4916	5.1	1.4830	29.2
IV	210	1.5009	0.5	1.5031	3.3	1.5046	6.2	1.4882	34.8
IV	215	1.5029	.3	1.5169	3.1	1.5068	6.6	1.4940	32.0
IV	220	1.5008	.2	1.5110	3.3	1.5044	6.5	1.4940	33.7
IV	225	1.5092	Trace		1.1	1.5252	8.9	1.4985	31.0
IV	230	1.5108	Trace		1.4	1.5348	8.6	1.5009	14.0
III	235	1.5050	None		1.5	1.5152	8.5	1.4997	15.0
IV	240	1.5090	0.2	1.5311	1.5	1.5342	8.3	1.5011	15.3
IV	245	1.5000	Trace		0.8	1.5190	9.2	1.4951	8.0
IV	250	1.5103	Trace		1.5	1.5326	8.5	1.5040	15.0
V	255	1.5137	Trace		1.3	1.5448	8.7	1.4960	13.0
IV	260	1.5138	Trace		1.0	1.5519	9.0	1.5064	10.0
V	265	1.5145	Trace		1.1	1.5565	8.9	1.5050	11.0
IV	270	1.5201			1.4	1.5690	8.6	1.5077	14.0
V	275	1.5262			1.9	1.5760	8.1	1.5107	19.0
IV	280	1.5330			2.3	1.5739	7.7	1.5151	23.0
V	285	1.5418			2.7	1.5733	7.3	1.5230	27.0
IV	288	1.5428			3.1	1.5709	6.9	1.5323	31.0
III	295	1.5468			3.0	1.5732	7.0	1.5311	30.0
III	300	1.5532			3.0	1.5755	7.0	1.5372	30.0
III	305	1.5545			3.1	1.5747	6.9	1.5382	31.0
II	310	1.5623			2.8	1.5755	7.2	1.5486	28.0
II	315	1.5640			2.6	1.5759	7.4	1.5496	26.0
II	320	1.5661			1.9	1.5745	8.1	1.5565	19.0
II	325	1.5662			1.7	1.5762	8.3	1.5561	17.0
II	330	1.5671			1.4	1.5758	8.6	1.5574	14.0
II	335	1.5718			1.0	1.5921	9.0	1.5598	10.0
II	345	1.5910			2.5	1.6200	7.5	1.5720	25.0
II	350	1.5768			1.5	1.6045	8.5	1.5650	15.0

Ten cc. samples from each of the above fractions, dissolved in 10 cc. of 1:1 hydrochloric acid, were carried through a single extraction with 20 cc. of chloroform and then the bases in the aqueous and chloroform layers were precipitated from the dissolved hydrochlorides with an excess of caustic soda. In some cases a small amount of hydrocarbon oil was encountered.

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[7] Ref. 4, p. 1243.

sulfate in acetone facilitated the separation from accompanying 2,3,8-trimethylquinoline. Final purification was effected through the picrate, which crystallizes from alcohol in slender rectangular plates melting at 193°.

The boiling point of 269–270° (pressure not given) for 2,4,8-trimethylquinoline, as recorded in the literature,[8] does not agree with our determination of 280° (corr.) at 746 mm. on both the synthetic product and the kero base. For this quinoline n_D^{50} is 1.5855.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.43; H, 7.42; N, 8.35.

Phthalone of 2,4,8-Trimethylquinoline.—The base and the calculated amount of phthalic anhydride are heated for three hours at 200°, the melt is dissolved in concentrated sulfuric acid and the solution is poured onto crushed ice. The phthalone crystallizes from alcohol in yellow microscopic needles melting at 282°.

Anal. Calcd. for $C_{20}H_{15}O_2N$: C, 79.73; H, 4.98; N, 4.65. Found: C, 79.65; H, 5.16; N, 4.71.

Comparative Efficiency of the Cumulative Extraction and Sulfur Dioxide Processes in Segregation of Aromatic Bases.—600 cc. of residual bases of the 263–267° fraction from which 2,3- and 2,4-dimethylquinoline had been isolated by the use of sulfur dioxide, as described in Paper V of this series, was carried through cumulative extraction. It developed that, whereas sulfur dioxide had removed 2,4-dimethylquinoline completely, an additional 5 g. of the 2,3-isomer could be recovered. The difficult solubility of the picrate of this base in alcohol simplified its purification. There was also encountered here in small amount a new $C_{12}H_{13}N$ base for which proof of structure and synthesis is under way.

Cumulative Extraction in Evaluation of the Nature and Amount of Aromatic Bases in Distillation Fraction.—The subjoined table gives the results from cumulative extraction of kero bases, within the b. p. range of 182–350°. The samples above 300° were imperfectly fractionated. It is probable that both aromatic and non-aromatic hydrochlorides of these bases exhibit within the two types a considerable variance in relative solubilities in water and chloroform, so frequently the initial chloroform extraction does not furnish a true picture of the proportionate amounts of the two types. However, from cumulative extraction when applied exhaustively—and this is possible with 10-cc. samples—estimates reliable within narrow limits of error can be reached.

The aromatic bases in the 182–220° fractions consist mainly of pyridine homologs, where an average n_D^{25} value[9] around 1.5000 may be expected. In fractions above 220° pyridines will probably not be encountered. Since quinoline homologs have an n_D^{20} value around 1.6000, the deduction follows from the data in Table I that fractions above 330° contain an appreciable quantity of aromatic bases of a higher order than quinolines.

Summary

Based on a wide difference in the distribution ratio of the hydrochlorides of aromatic and non-aromatic petroleum bases between water and chloroform, a method of segregation of the two types, for which the name "Cumulative Extraction" is proposed, has been developed. This process is now a standardized and reliable procedure of general application. The isolation by this method of 2,4,8-trimethylquinoline and a second $C_{12}H_{13}N$ base of unknown structure is described.

AUSTIN, TEXAS
RECEIVED MARCH 20, 1933
PUBLISHED OCTOBER 6, 1933

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[8] S. Yamaguchi, *J. Pharm. Soc., Japan*, pp. 5–6 (1924); *Chem. Zentr.*, **98**, 1837 (1927).

[9] *Cf.* Takashi Eguchi, *Bull. Chem. Soc. Japan*, **3**, 241 (1928).