The following blank values were subtracted from the observed reducing values to correct for the non-removable reducing material introduced by the nitrogen–ethylene quenching process.

Solution	"Initial reducing value," mg. iodine/100 mg. sample	Alkali-labile value, mg. iodine/100 mg. sample
Unbuffered chlorine water	0.02 ± 0.01	0.08 ± 0.02
Chlorine water buffered by phosphate	0.04 ± 0.01	0.05 ± 0.01
Alkaline hypochlorite solution	0.02 ± 0.01	0.08 ± 0.01

The hydrolysis of β-amylose dispersions was carried out as follows: 5.00 cc. of the chlorine-treated solution containing 1.000 g. of carbohydrate per 100 cc. of solution of *p*H 7 were pipetted into a Pyrex test-tube and mixed with 5 cc. of 2 *M* hydrochloric acid. The mixture was heated in a boiling water-bath for thirty-five minutes, cooled, almost neutralized with almost saturated sodium hydroxide solution and accurately neutralized with 0.1 *N* alkali to nitrazine yellow. The "initial reducing value" was then determined as usual.

Acknowledgment.—The authors wish to thank Prof. J. M. Nelson, Dr. A. F. Knoll and Dr. C. O. Beckmann for their valuable assistance in preparing this paper. They are grateful also to Dr. H. B. Hardt for carrying out the *p*H measurements, using the glass electrode circuit of Ellis and Kiehl.[33]

---

(33) Ellis and Kiehl, *Rev. Sci. Instruments*, **4**, 131 (1933).

Summary

1. The action of chlorine water and of alkaline hypochlorite on β-amylose has been followed quantitatively throughout its course at room temperature by measurement of the reducing power and viscosity of the β-amylose.

2. In alkaline medium the reaction is primarily an oxidation of the aldehyde groups at the ends of the glucoside chains, but is accompanied by some disintegration of the carbohydrate.

3. In acid medium the reaction proceeds differently. After a short time during which no apparent reaction occurs there is a sudden rise in reducing power and simultaneous drop in viscosity. If the acid generated during the reaction is neutralized this abrupt reaction is followed gradually by a complete breakdown of the carbohydrate to products without reducing action toward alkaline hypoiodite reagent.

4. These changes in the reducing power and viscosity can be explained easily by assuming that β-amylose exists in the form of the micelle postulated by Meyer and Mark.

5. A rapid method for the quantitative removal of hypochlorous acid from aqueous solutions has been described.

NEW YORK, N. Y. RECEIVED APRIL 5, 1938

[CONTRIBUTION NO. 132 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

Nitrogen Compounds from Petroleum Distillates. XII. Fractional Sulfiting of Bases and Fractional Degassing of their Acid Sulfites[1,2]

BY STILES M. ROBERTS AND J. R. BAILEY

Introduction

It is well known that acid sulfites of organic nitrogen bases dissociate on heating their aqueous solutions into base, sulfur dioxide and water.

$$\text{Base } H_2SO_3 \longrightarrow \text{Base} + SO_2 + H_2O$$

In this paper, there is described how, by employing the velocity of dissociation of acid sulfites at variable temperature levels, a process of "Fractional Degassing" has been developed which can be used to advantage in resolution or organic nitrogen base mixtures into component types. This procedure is applicable especially to petroleum and coal tar base fractions.

As an experimental background for the process, a crude fraction of kero bases (kerosene bases) in the 270–280° boiling range was selected. Here have been isolated previously 2,3- and 2,4-dimethylquinoline,[3] 2,3,8-trimethylquinoline,[4] 2,4,-8-trimethylquinoline,[5] and a $C_{16}H_{25}N$ naphthenic base.[6]

The 270–280° fraction of kero bases may be arranged in three different types.

---

(1) Presented before the Petroleum Division of the American Chemical Society, Dallas, Texas, April 19, 1938.

(2) "Sulfiting" implies conversion of bases to acid sulfites and "degassing" implies dissociation of the acid sulfites with the liberation of free bases and sulfur dioxide.

(3) Burnard S. Biggs and J. R. Bailey, THIS JOURNAL, **55**, 4141 (1933).

(4) W. A. King and J. R. Bailey, *ibid.*, **52**, 1245 (1930).

(5) T. S. Perrin and J. R. Bailey, *ibid.*, **55**, 4136 (1933).

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

A	B	C
Aromatics Two di- and two trimethylquinolines	A $C_{16}H_{25}N$ base, probably of naphthenic structure	A complex mixture of unknown composition and representing about 70% of this fraction

The velocities of degassing at 33° of the A, B and C components are in the approximate order of 1:9:30. After degassing had practically ceased at this temperature level, it was continued by progressively raising the temperature of the sulfite brine. Around 80° evolution of sulfur dioxide stopped abruptly, although it was known that the component base acid sulfites degas readily at this temperature. The inhibition to degassing was revealed in that qualitative tests were negative for *sulfites* and positive for *sulfates*. This observation suggested that the oxidizing effect of aeration could be circumvented by carrying out degassing with the aid of inert gases such as nitrogen, carbon dioxide or natural gas. This forecast has been confirmed experimentally.

Fractional sulfiting, as shown in the Experimental Part, is comparable in efficiency to degassing and was tried on the same material as was used in the latter process. Since a combination of the two methods involves the *use* of sulfur dioxide in the first phase and its *recovery* in the second phase, an economical and practical cyclic method of resolution of base mixtures, without any consumption of chemicals, is presented.

Our results and the results of Axe and Bailey (see following paper) emphasize how cumulative extraction[5] supplements in a favorable way sulfiting and degassing in processing petroleum base fractions of straight-run distillates.

Experimental Part

Degassing Acid Sulfites of the 270-280° Kero Base Fraction.—Into a mixture of 1 liter of bases and 3 liters of water sulfur dioxide is led until complete solution results. Through this solution cooled to 20°, air is passed at approximately 0.5 liter per minute until evolution of sulfur dioxide practically ceases. The bases which layer out as a supernatant oil were withdrawn in seven fractions ranging from 20 to 147 cc., as shown in Table I. The degassing proceeded rapidly for some time and then slowed down progressively, as can be inferred from twenty-four hours being required for the separation of fraction 7 (20 cc.). Fraction 8 required three hours of degassing at 50° and fraction 9 required six hours at 80° when, due to a complete sulfite–sulfate conversion, the evolution of sulfur dioxide ceased.

From fraction 9 there separated 2 g. of a crystalline salt which yielded, on treatment with sodium hydroxide, 2,3,8-trimethylquinoline. The latter was identified by the usual comparison with an authentic sample.

TABLE I

DEGASSING OF BASES OF 270–280° BOILING RANGE

Fraction	Temp. of brine, °C.	Vol., cc.	n^{25}_D
1	20	59	1.5132
2	20	105	1.5183
3	20	70	1.5214
4	20	147	1.5258
5	20	40	1.5263
6	20	32	1.5276
7	20	20	1.5281
8	50	96	1.5277
9	80	18	1.5281
Residual bases from sulfates		413	1.5303
Original bases		1000	1.5267

The bases (413 cc.) recovered from the residual sulfate brine (fraction 9) were dissolved in 240 cc. of 6 *N* hydrochloric acid and seeded with 2,3,8-trimethylquinoline hydrochloride. After eighteen hours in the ice-box, 12 g. of the pure hydrochloride had separated. This characteristic salt is difficultly soluble in water as compared with the hydrochlorides of the associated kero quinolines.

The smeary residue obtained by evaporation of the filtrate was washed with five portions of hot acetone (total 75 cc.) and the bases (n^{20}_D 1.5142) were recovered from the solvent. The acetone insoluble hydrochlorides yielded 53 cc. of bases (n^{20}_D 1.5228) which were further processed through cumulative extraction.[5]

The n^{20}_D values, 1.5143 and 1.5501, of 22 cc. from the chloroform layer, and 30 cc. from the water layer, respectively, emphasize the efficiency of cumulative extraction in combination with sulfiting and degassing.

Table II comprises degassing data on the acid sulfite solutions of base fractions 1, 2 and 8 (Table I).

TABLE II

Source of acid sulfite	Fraction	Degassing temp. of brine, °C.	Bases liberated Vol., cc.	Bases liberated n^{20}_D
A composite of fraction 1 and 2.	1a	0	28	1.5086
	2a	0	25	1.5120
	3a	20	25	1.5152
	4a	20	19	1.5175
	5a	20	9	1.5208
	6a	..	22	1.5300
Fraction 8	1b	20	16	1.5197
	2b	20	13	1.5203
	3b	20	25	1.5218
	4b	..	42	1.5303

The residual fractions 6a and 4b underwent sulfite-sulfate conversion. However, from 6a, there separated on standing a crystalline acid sulfite from which 7 g. of 2,3,8-trimethylquinoline was obtained. Here the residue, from the evaporation of the filtrate and leaching out the smeary residue with cold acetone, yielded an additional 3 g. of the same acid sulfite.

Fractional Sulfiting of the 270–280° Kero Base Fraction.—One liter of bases was fractionally neutralized with 100-cc. portions of 8% aqueous sulfurous acid under vigor-

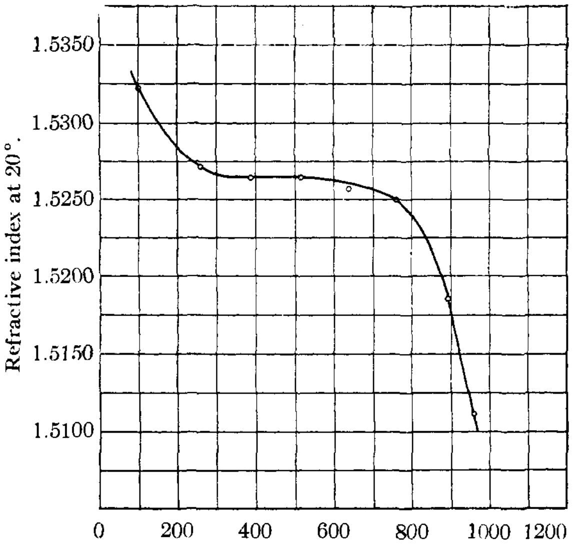

Fig. 1.—Sulfiting of crude base fraction.

ous agitation over ninety-minute periods. At the end of each extraction the aqueous layer was drawn off and the bases were liberated. The results obtained are presented in Table III.

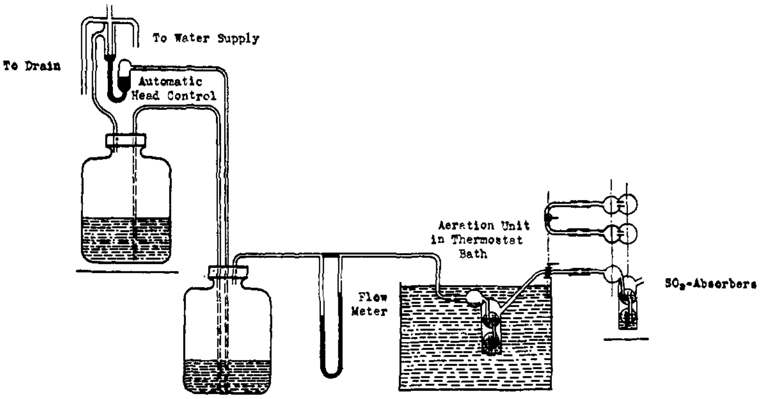

Fig. 2.—Apparatus for determination of degassing rates.

The recombinations, A, B and C, of the nine fractions corresponding to the three pronounced slopes in Fig. 1, were further processed through cumulative extraction by agitation for several hours of the base fractions, with 6 *N* hydrochloric acid and chloroform in the volume ratio of 1:1:1.2, respectively. The results are presented in Table IV.

Since a crystalline hydrochloride separated from the aqueous layer of both B and C before liberation of the bases, the 25-cc. and the 17-cc. fractions were reconverted to the hydrochlorides with the result that 7 and 3 g., respectively, of pure 2,3,8-trimethylquinoline as hydrochloride precipitated. The refractivity of the 66 cc. of non-aromatics from **B** approached that of the $C_{16}H_{25}N$ base ($n^{20}D$ 1.5129). In order to confirm the presence of this substance, this fraction was converted to anhydrous hydrochlorides, smeary admixtures were leached out with cold acetone, and the crystalline residue was extracted with 400 cc. of hot acetone. After filtering off the undissolved hydrochlorides, the filtrate was concentrated to a small volume, whereupon 17 g. of practically pure $C_{16}H_{25}N \cdot HCl$ separated.

TABLE III

FRACTIONAL ACID EXTRACTION WITH SULFUROUS ACID

Fraction	Vol. of bases from extract, cc.	$n^{20}D$	
1	95	1.5322	A
2	160	1.5272	
3	130	1.5265	B
4	130	1.5265	
5	120	1.5256	
6	125	1.5250	C
7	130	1.5186	
8	70	1.5112	

TABLE IV

CUMULATIVE EXTRACTION OF BASES FOLLOWING FRACTIONAL ACID EXTRACTION

			Bases from water layer		Bases from chloroform layer	
Combination	$n^{20}D$	Vol. used, cc.	Vol., cc.	$n^{20}D$	Vol., cc.	$n^{20}D$
A	1.5316	100	27	1.5721	73	1.5174
B	1.5258	100	25	1.5614	66	1.5120
C	1.5222	100	17	1.5624	82	1.5090

Determination of Dissociation Rates of Base Acid Sulfites.—In order to make a thorough study of the rate of dissociation of acid sulfites of nitrogen bases, a method was devised whereby solutions of the salts could be used even though there were present an undetermined excess of sulfur dioxide. This scheme was effected by consideration of the difference in the rate of evolution of sulfur dioxide during degassing from solutions containing (1) an insufficiency and (2) an excess of sulfur dioxide for salification of the base.

Through 10 cc. of an aqueous solution of a weighed quantity of base in an excess of sulfurous acid a quantity of air is passed at a constant rate (see Fig. 2). The vapor from the aeration unit is led into the sulfur di-

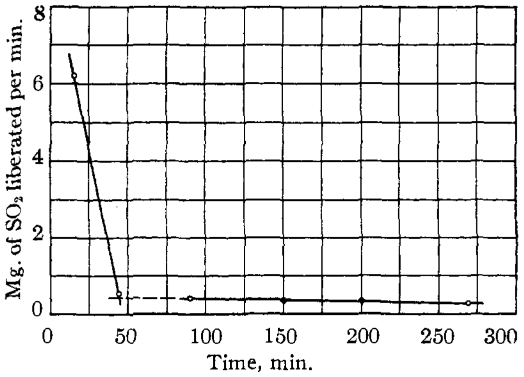

Fig. 3.—Degassing rate of the $C_{16}H_{25}N$ base acid sulfite.

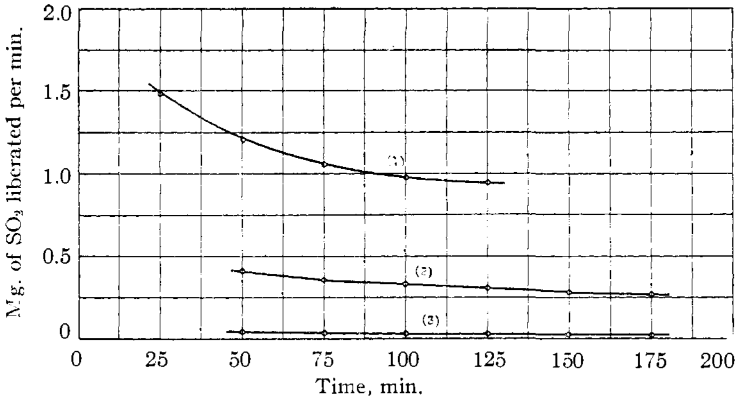

Fig. 4.—Comparison of degassing rates of: (1) non-aromatic fraction, (2) the $C_{16}H_{25}N$ naphthenic base and (3) quinoline acid sulfites.

oxide absorber containing 40% potassium hydroxide. Two absorbers, operating alternately at recorded intervals of time, are connected to the aeration unit through a two-way stopcock so that the rate of degassing can be followed without interruption. The absorbed sulfur dioxide is determined iodometrically. In a series of experiments involving three different bases, the rates of sulfur dioxide evolution from the aeration unit are deduced and plotted against time. At the inflection point of each curve, it is assumed, all of the *excess* sulfur dioxide—*and only the excess*—is removed, leaving behind only base acid sulfite. By shifting the time abscissa of the curve for each base so that the inflection points coincide, a composite set of curves follows whereby a comparison of the degassing rates is presented. Figure 3 shows the degassing rate of the $C_{16}H_{25}N$ naphthenic base. Figure 4 derived from Fig. 3, along with similar curves for quinoline and a complex non-aromatic fraction (b. p. 270–280°), denotes the comparative degassing rates of their acid sulfites.

Summary

Experience has demonstrated that, by following the old beaten track in processing coal tar bases, which are essentially of aromatic character, not much progress can be expected in isolation of the components of the far more complex straight-run petroleum base fractions.

In the present investigation, a new cyclic process of resolution is described which employs the reversible reaction

$$\text{(A) Base} + SO_2 + H_2O \underset{\text{Degassing}}{\overset{\text{Sulfiting}}{\rightleftarrows}} \text{(B) Base}\cdot H_2SO_3$$

In (A), fractional acid extraction and in (B), fractional acid-sulfite dissociation are involved.

It was beyond the scope of the present investigation to effect quantitative separations of the known components of the complex mixture of the bases processed; on the contrary, the aim was to establish Fractional Sulfiting and Fractional Degassing as general procedures which can contribute to an extension of the chemistry of petroleum bases.

AUSTIN, TEXAS RECEIVED JUNE 2, 1938

[CONTRIBUTION NO. 133 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XIII. Isolation of Four Quinoline Homologs and Two Aromatic Bases of Probable Trinuclear Cyclic Structure[1]

BY W. NELSON AXE[2] AND J. R. BAILEY

Introduction

The main objective of this investigation concerned the isolation of aromatics in the 300° range of kero bases. In refining the crude material, the following steps were involved: (1) fractional acid extraction followed by a rough distillation; (2) fractional distillation of the desired cuts from (1) after appropriate recombinations in the order of boiling points and refractive indices; (3) cumulative extraction[3] of fractions from (2) preceded by the usual recombinations; (4) fractional distillation of the aromatic bases which were concentrated as hydrochlorides in the aqueous layer in step 3.

Attempts to isolate individual components in fractions from step 4 around the 295° boiling range were rewarded by the recovery of two products in poor yield of the composition $C_{13}H_{15}N$ (I) and $C_{14}H_{17}N$ (II) through fractional precipitation and recrystallization of different salts. Further work on these compounds awaits the assembling of sufficient quantities for proof of structure.

Since the results reported above were disappointing, resort was had to degassing of acid sul-

---

[1] Presented before the Petroleum Division of the American Chemical Society, Dallas, Texas, April 19, 1938.

[2] From a dissertation presented by W. N. Axe to the Faculty of the Graduate School of The University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Perrin and Bailey, THIS JOURNAL, **55**, 4136 (1933).