[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE RICE INSTITUTE]

Acidic Constituents of a West Texas Pressure Distillate

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Notwithstanding the vast amount of petroleum that is produced in the state of Texas, little work of purely scientific nature has been done on the chemical composition of either Texas crude or refinery products derived from it. Chemical literature is particularly meager in information relating to the components of the acidic fractions, although numerous investigations have been carried out on the acidic constituents of other, especially the Russian, oils for the past several decades.

The object of the work described in the following sections was the determination of the type of acids present in a Texas naphthenic acid fraction. A sample of commercial naphthenic acids from the alkali wash of a Dubbs pressure distillate was furnished for the investigation by a local refinery. The charge to the pressure still was the gas oil fraction of a West Texas crude.

Experimental

(1) **Preliminary Separation.**—Several liters of the crude acids were dissolved in dilute sodium hydroxide and subjected to steam distillation; the distillate (I) and the non-volatile residue (II) were then examined. The non-volatile portion (II) was treated with sulfuric acid to liberate the organic acids and steam distilled; these acids were converted into the methyl esters (III). The impure methyl esters upon extraction with sodium hydroxide separated into the alkali-soluble phenols (IV) and the semi-pure esters (V).

(2) **Examination of I.**—This material is principally the petroleum hydrocarbons which were emulsified in the original acids; it contains a small amount of mercaptan and phenols.

In order to isolate the sulfur constituents, some of the material was treated with an alcoholic solution of mercuric chloride, the precipitate being collected and suspended in dry ether; the original sulfur compounds were liberated by hydrogen sulfide. Extraction of the ether solution with potassium hydroxide removed all the odor, suggesting that neutral sulfur compounds were not present.

The mercaptan boiled at 35–37° and on treatment with alcoholic mercuric cyanide the mercury salt, m. p. 76–78° was obtained, which corresponds to that of ethyl mercaptan. The silver salt was prepared and analyzed by Pregl's method.

Anal. Calcd. for C_2H_5SAg: Ag, 63.84. Found: Ag, 63.77.

(3) **Examination of II.**—This fraction decolorized permanganate solutions, reacted with bromine in carbon tetrachloride with evolution of hydrobromic acid, gave typical color reactions with ferric chloride and liberated carbon dioxide from sodium bicarbonate. This portion is obviously a mixture of phenols and carboxylic acids.

This material was mixed with two parts of methyl alcohol and refluxed for several hours in the presence of sulfuric acid. The excess alcohol was removed by distillation and the residue poured into dilute alkali; the insoluble esters (V) were separated and dried. The phenols recovered from the alkaline wash solution were combined with the ethereal extract of the water obtained from (I).

(4) **Examination of IV.**—The combined phenolic fraction, which contained a small amount of aliphatic acids, was then fractionated in a column constructed after the design of Peters and Baker. Five fractions were obtained: (1) 175–181°, (2) 181–185°, (3) 190–192°, (4) 201–202°, (5) 212–218°.

The examination of fraction (1) gave evidence that it was a mixture of a phenol and a carboxylic acid; these were separated by extracting with sodium bicarbonate solution. The acid boiled at 172–176°. The silver salt of the crude acid was prepared and analyzed.

Anal. Calcd. for $C_5H_9O_2Ag$: Ag, 51.7. Found: Ag, 52.2.

Since the odor and equivalent weight suggested that the compound was valeric acid the amide was prepared for confirmation. The amide melted at 125–130° which corresponds to isovaleramide, m. p. 126–128°.

The second cut could not be purified by further distillation so recourse to a partial solution procedure was resorted to by extracting with large volumes of water. The aqueous solution was treated with bromine, a voluminous white precipitate being thrown down. After several recrystallizations the product melted at 90–93°. This material was evidently the tribromo derivative of phenol. Confirmation was obtained by determining the mixed melting points with a known sample of tribromophenol, mixed melting point, 92–93°.

As has been noted, both Japanese and Russian petroleums, as investigated by Tanaka and Kobayshi,[1] and Holzman and Pilat,[2] respectively, contained no phenol. While the amount of phenol in the sample under consideration was undeniably small, the evidence of its presence cited above may be considered as fairly conclusive.

Fraction (3), b. p. 190–192°, d^{20}_{20} 1.052, indicated *o*-cresol as the most likely possibility. This was confirmed by conversion into the aryloxyacetic acid, which, after three recrystallizations, melted at 150–152° (*o*-cresyloxyacetic acid, m. p. 151–152°).

Fraction (4), b. p. 201–203°, corresponds to either one, or a mixture of *m*-cresol and *p*-cresol. The identification of the *p*-cresol was made by the aryloxyacetic acid derivative, which, after repeated recrystallizations, melted at 123–127°. Use was made of the characteristic trinitro

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(1) Tanaka and Kobayshi, *J. Faculty of Science*, Imperial Univ. of Tokyo, **17**, 127 (1927).

(2) Holzman and Pilat, *Brennstoff-Chem.*, **11**, 409 (1930).

derivative of the *m*-cresol for its identification, m. p. 105°. This fraction was principally *m*-cresol.

The fraction of phenols boiling at 212–218° evidently consisted of one or more xylenols. Since the boiling points of the six isomeric xylenols range from 212 to 225° and coincide for several isomers, it is practically impossible to effect a clean-cut separation by distillation. The aryloxyacetic acid derivative of the entire cut was therefore prepared in the hope that one individual would predominate. Several recrystallizations gave a product of constant melting point, 86–88°. This corresponds to the melting point of the 1,3,5-xylenol derivative.[3] This material has been found in Russian and Japanese petroleums by Holzman and Pilat[2] and Tanaka and Kobayshi.[1]

Refractionation of the cut taken at 210–212° gave 5 cc. of a constant boiling liquid. This was converted into the aryloxyacetic acid and the product recrystallized fifteen times until no change in melting point was evident upon further recrystallization. The melting point of 118° coincides with that of the aryloxyacetic acid derivative of 1,2,4-xylenol.

(5) **Examination of V.**—The esters obtained from the phenol mixture mentioned above were washed thoroughly and dried over calcium chloride. The mixture was then distilled through the column previously mentioned at a pressure of 1.2 mm. The boiling range was 48–90°; five cuts were separated which corresponded to the "flats" on the distillation curve.

Since the various fractions all possessed a typical phenol odor, each fraction was washed with dilute alkali. Each part was then tested for the presence of phenols by the Liebermann reaction and by coupling with diazotized sulfanilic acid; the washing was repeated until the phenols were removed.

The first fraction of esters was refractionated several times in a small Vigreux flask, and a small cut boiling at 45.2–46.0° under 1.2 mm. was obtained. This was hydrolyzed with alcoholic potassium hydroxide. The acid obtained from the hydrolysis, on subsequent fractionation, gave a small fraction of *o*-cresol and a fraction boiling at 88–88.5° at 2 mm. which was free from phenols, as shown by failure to discolor bromine water. Micro analyses of the silver salt of this material gave 45.27 and 44.62% Ag, corresponding to a molecular weight of 132. The acid was further distilled and the silver salt analyzed until it reached a constant composition. The free acid was then analyzed to determine the empirical formula.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Calcd. for $C_7H_{12}O_2$: C, 65.57; H, 9.45. Found: C, 64.40; H, 10.36.

Anal. Calcd. for $C_7H_{13}O_2Ag$: Ag, 45.54. Found: Ag, 45.60.

From the above results the acid evidently has the empirical formula $C_7H_{14}O_2$: it is an aliphatic, rather than a cyclic or naphthenic acid. The boiling point was found to be 220.5 at 770 mm., d^{23}_{0} 0.925. This substance was thought to be *n*-heptylic acid.

In order to determine whether or not the acid isolated was identical with the normal acid, the *p*-bromophenacyl ester was prepared from both the acid isolated and a sample of known *n*-heptylic acid. The known sample melted at 71.5°, the unknown preparation melted at 70°. The mixed melting point was 70–71°. This acid may well be identical with that described by Tschitschibabin.[4] His acid boiled at 215–218° and on combustion gave an identical empirical formula. The structure provisionally assigned to it, that of either isoheptylic or β,β-diethylpropionic acid, was based on the apparent presence of a secondary or tertiary carbon atom in the molecule. However, the inaccessibility of his data does not permit further comparison.

The second ester fraction boiling from 55–59° under 1.2 mm. was repeatedly fractionated and hydrolyzed. The acid so obtained was fractionated in a Vigreux flask; the distillate did not discolor bromine in carbon tetrachloride. The cut boiling at 87–87.5° under 1.3 mm. was examined. The boiling point at atmospheric pressure was 235.5°. The silver salt of this acid was prepared and micro combustion of the salt carried out.

Anal. Calcd. for $C_8H_{15}O_2Ag$: C, 38.24; H, 6.02; Ag, 43.00. Found: C, 38.36; H, 6.04; Ag, 42.86.

The *p*-bromophenacyl ester was prepared for characterization. Derivatives of both the unknown acid and known *n*-octylic acid were prepared. The ester of the acid isolated melted at 63–65°; mixed melting point of the known and unknown samples was 65–66°. Hence this acid is *n*-octylic acid.

The third cut of esters boiling from 60–62° under 1.2 mm. was refractionated several times and hydrolyzed with alcoholic potassium hydroxide. The impure acid isolated was then refractionated until an apparently pure fraction boiling at 95.5–97.5° at 2 mm. was obtained. This material was practically free from phenols as shown by the bromine test. The analysis of the silver salt revealed that the acid was a mixture of two homologs. Working with larger samples, *n*-octylic acid and a new acid boiling at 101–103° under 2 mm. were separated from this mixture. The latter substance exhibited a faint reaction with bromine. Silver salt analysis indicated an equivalent weight of 159.3. Micro combustion of the salt gave the following values.

Anal. Calcd. for $C_9H_{17}O_2Ag$: C, 40.76; H, 6.47; Ag, 40.70. Found: C, 41.08; H, 6.27; Ag, 40.51.

The boiling point of this compound under atmospheric pressure was 251.5°; d^{27}_{0} 0.929. *n*-Nonylic acid boils at 252°; d^{20}_{0} 0.906. Despite the differences in densities, which in all probability was due to the presence of a small amount of phenols, it seemed likely that the acid isolated was the normal compound. Confirmation was obtained by the use of the *p*-bromophenacyl ester as a derivative which melted at 62–64°; mixed melting point with *p*-bromophenacyl ester of pelargonic acid, 63–65°. Higher ester fractions than those containing methyl pelargonate were hydrolyzed in the hope of isolating higher homologs, but none of these were obtained in a pure enough state to warrant analysis.

A rough semi-quantitative examination of the mixture was made to determine the approximate amounts of the individuals present. This was accomplished by graphical analysis of the distillation curves of the purified material and by measuring the volume of the products isolated.

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(3) Meyer, "Nachweis und Bestimmung organischer Verbindung."

(4) Tschitschibabin, *Dokladui Akd. Nauk S. S. S. R.*, A, 382 (1930).

1750 cc. of the crude acids on alkaline steam distillation gave 200 cc. of neutral oil (11%) and 5–10 cc. of ethyl mercaptan (0.6%) as the distillate. The residue of 1500 cc. (86%) was esterified with methyl alcohol and extracted with ether from alkaline solution. 250 cc. of esters (15%) was separated from 1050 cc. of phenols (71%). The phenols on distillation gave 500 cc., b. p. 190–230° (34%). 75 cc., b. p. 230–265° (4%) and 400 cc. of tar (23%). The first phenolic fraction on subsequent distillation yielded 145 cc. of *o*-cresol (8%). 135 cc. of a mixture of *m*- and *p*-cresols (8%), 60 cc. of undetermined (3%) and 180 cc. of xylenols (10%).

Summary

1. Commercial naphthenic acids from a West Texas pressure distillate were shown to consist for the most part of phenolic constituents.

2. The following compounds have been isolated and identified from the sample: ethyl mercaptan, phenol, *o*-cresol, *m*-cresol, *p*-cresol, 1,3,5-xylenol, 1,4,2-xylenol, isovaleric acid, *n*-heptylic acid, *n*-octylic acid and *n*-nonylic acid.

3. The finding of aliphatic acids and of no cyclic acids tends to throw doubt on the claims of earlier investigators who reported the cyclic compounds exclusively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Electron-Sharing Ability of Organic Radicals. IX. Dissociation Constants of Amines and Acids in Ethanol

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The dissociation constants of a series of organic acids and amines in methanol, as measured by the hydrogen electrode, were reported in a previous paper.[1] The constants measured in methanol by the hydrogen electrode were found to agree favorably with the values obtained by Goldschmidt[2] using conductimetric methods. Similar measurements for ethanol solutions are reported in this publication.

Experimental

The resistance of the ethanol solutions was so great that it was necessary to use a vacuum tube null-instrument in the place of the vacuum tube potentiometer[3] used with methanol solutions. An apparatus constructed similar to the one described by Ellis and Kiehl[4] gave convenient measurements with a precision of 0.1 millivolt. All measurements were made in an air-bath maintained at 25 ± 0.1°. A wire screen inside of the cabinet was necessary to prevent electrical disturbances from being transmitted to the vacuum tube measuring instrument.

The standard electrode potential of the silver–silver chloride electrode in ethanol has been reported by MacFarlane and Hartley.[5] The activity of hydrogen chloride in alcohol has been determined by Danner,[6] by Harned and Fleyscher,[7] and by Woolcock and Hartley.[8] With these values known the hydrogen-ion activity of an unknown solution can be measured by using either the silver–silver chloride or the hydrogen half-cell as a reference electrode.

Although the silver–silver chloride electrodes are reproducible, they are inconvenient to use as reference cells due to the great care required in their preparation and the fact that a freshly prepared electrode must be used for each measurement. Mercury–mercuric iodide half cells in alcoholic potassium iodide have been used by Johns and Hixon[9] with flowing junctions to eliminate polarization. Using a static junction through a glass stopcock, the voltage of the concentration cell

$$\mathrm{Hg/HgI_2\ (0.005\ \mathit{m})\ KI\ (0.05\ \mathit{m})//KI\ (0.05\ \mathit{m})\ HgI_2\ (0.01\ \mathit{m})/Hg}$$

was found to be 0.0146 volt as compared with the value 0.01455 volt reported by the former investigators using flowing junctions. These half-cells remained constant almost six months during the period of observation. The voltage of these half cells referred to the normal hydrogen electrode in alcohol was determined by measurement against the silver–silver chloride electrode

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[1] Goodhue and Hixon, THIS JOURNAL, **56**, 1329 (1934).

[2] Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921); Goldschmidt and Aas, *ibid.*, **112**, 423 (1924); Goldschmidt and Mathiesen, *ibid.*, **119**, 439 (1926).

[3] Goodhue, Schwarte and Fulmer, *Iowa State College J. Sci.*, **7**, 111 (1933).

[4] Ellis and Kiehl, *Rev. Sci. Inst.*, **4**, 131 (1933).

[5] MacFarlane and Hartley, *Phil. Mag.* [7] **13**, 425 (1932).

[6] Danner, THIS JOURNAL, **44**, 2832 (1922).

[7] Harned and Fleyscher, *ibid.*, **47**, 82 (1925).

[8] Woolcock and Hartley, *Phil. Mag.*, [7] **5**, 1133 (1928).

[9] Johns and Hixon, *J. Phys. Chem.*, **34**, 2226 (1930).