Compound b (Formula IV, $C_{12}H_{16}$), in its behavior with bromine, its molecular refractivity and its magnetic rotatory power, acts consistently as though containing two systems of conjugated double bonds.

Compounds c (Formulas VI and VIII, $C_{12}H_{18}$) act towards bromine like substances containing conjugated double bonds such as to cause nuclear addition and not simple addition to side chains, although no pure bromine derivatives could be isolated. In their molecular refractivities and magnetic rotatory powers, they resemble $\Delta^{1,3}$-dihydrobenzene.

A dynamic representation of benzenoid structure, similar to that proposed by Collie,[1] which includes different static formulas as phases of its vibration, lends itself best to the interpretation of the behavior of the hydrocarbons described above.

Summary.

1. Unsaturated hydrocarbons, related to the terpenes, have been prepared by the action of methyl magnesium iodide upon methyl terephthalate and its di- and tetrahydro derivatives.
2. The new compounds prepared were the 1,4-diisopropenyl benzene ($C_{12}H_{14}$); 1,4-diisopropenyl-$\Delta^{1,4}$-dihydrobenzene ($C_{12}H_{16}$); 1,4-diisopropenyl-Δ^{1}-tetrahydrobenzene ($C_{12}H_{18}$), or an isomer thereof; tetramethyl *p*-phenylene glycol; and certain bromine addition products of the new hydrocarbons.
3. The refractivities and magnetic rotatory powers of the new hydrocarbons, as well as their densities, have been determined and are discussed with reference to their bearing upon the structures assigned to these compounds.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

THE GENESIS OF PETROLEUM AS REVEALED BY ITS NITROGEN CONSTITUENTS.

BY CHARLES F. MABERY.

Received July 26, 1919.

From what is known concerning natural processes of building up complex nitrogen organic compounds they are limited to the agency of vegetable or animal life. The circuitous laboratory methods leading through many changes to intricate structure have no counterpart in nature except through the influence of the life principle. If, therefore, such nitrogen derivatives are universally present in petroleum it is difficult to avoid the conviction that these bodies had their origin as evolution products of organic life, and that the hydrocarbons with which they are associated were evolved from the same source. The universal presence of nitrogen

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[1] *J. Chem. Soc.*, **71**, 1013 (1897).

compounds thus becomes of considerable interest as a determining feature of the genesis of petroleum especially since several of the heavier varieties, notably those from the California and Russian fields have been found to contain nitrogen compounds in large proportions. In a wide area of the California fields sufficient organic débris has been disclosed to account for all the oil in that region. The great deposits of petroleum here are unique in their conformation, and in respect to the nature of the oil are most interesting from the point of view of its composition. Like the immense stores in the Trenton Limestone of Ohio and Indiana the residual material from which it was formed is close at hand. Recent discoveries in California by Dr. Dickinson, of the "Martinez" beds of the Iocene period has revealed in a broad expanse of marine shell life, 4000 feet thick, an abundant supply of organic material for the origin of all the oil in those great fields. In view of the immense production of petroleum in Russia, chiefly at Baku and Bibi-Eibat, it is surprising that the Russian government has made no investigation of its origin nor of the geological conditions of its formation. Were it not for the assiduous labor of Mr. A. Beeby Thompson who spent several years in those oil fields as an engineer in the interests of European promotors nothing would be known concerning them. The results of his observations are published in a book entitled "The Oil Fields of Russia," London, 1904. In describing the oil sands and associated rock strata, Thompson denies an inorganic origin for Russian oil; vegetable matter he regards as doubtful, but animal or marine remains as the more probable source.

Of the numerous speculative suggestions relating to the genesis of petroleum, its formation from carbides in the hot regions of the earth's interior is perhaps the most plausible, for in the laboratory through acetylene hydrocarbons may be synthesized from metallic carbides. Assuming, however, such questionable formation of carbides, and the subsequent synthesis of petroleum hydrocarbons, it is scarcely conceivable that those hydrocarbons could withstand intimate contact with other volcanic vapors, nor the intense heat of volcanic conditions which has been suggested as the means of their transference to the geologic strata where petroleum is found. Still less could the unstable nitrogen derivatives of these hydrocarbons, if their similar synthesis could be imagined, survive exposure to such destructive conditions. The only possible source of these bodies was organic matter imbedded in the rock strata, and their solution in petroleum if formed from carbides could have resulted only from contact with infiltrated liquid hydrocarbons.

The heavier varieties of petroleum in the California, Texas, Ohio, Canada, Russian and similar fields, are complex mixtures of the denser hydrocarbons with oxygen, sulfur and nitrogen derivatives. They all differ widely in composition from the lighter varieties in the Eastern territory of the

United States, Pennsylvania, W. Virginia and the Berea Grit of Southern Ohio, which are fairly pure mixtures of two or three series of hydrocarbons, those of the series, C_nH_{2n+2} predominating. On account of the present isolation of the latter from carbonaceous matter that could in any manner be associated with their origin, except contiguous beds of coal, their source is not so readily apparent as that of other deposits. While they are for the most part free from sulfur, minute traces of the aromatic hydrocarbons, and oxygen derivatives are generally to be found, and nitrogen derivatives as shown by results to be described in this paper, are apparently everywhere present.

For a more extended discussion of what is here presented, as an introduction to the experimental results of this paper, reference is made to former papers.[1]

That nitrogen bases are generally present in Japan petroleum was shown by Mabery and Takano[2] who found in many samples from different fields, percentages of nitrogen varying from 0.35 to 1.5%. The wide distribution of these bodies in California petroleum appeared in the analysis of 16 samples from as many different fields that gave amounts from 1.0 to 2.55%. Ten samples of Ohio-Trenton Limestone petroleum gave percentages between 0.23 and 0.55%. Engler[3] enumerated the foreign petroleum fields where nitrogen bases have been identified—Germany, Galacia, Rumania, Sumatra, South America, Egypt and Algiers, showing their wide distribution.

These bases have been variously referred to as pyridine and quinoline or their derivatives by those who have separated them, more especially on account of their peculiar odor, and their general properties. In a more extended examination of the basic oil extracted from California petroleum, a series of bases were separated that appeared to be hydroderivatives of methyl quinolines,[4] but further study of their structure two years ago, undertaken in this laboratory at my suggestion by Dr. L. G. Wesson, the results of which are not yet published, appears to indicate that these individual bases are straight methyl quinolines.

With the object in view of demonstrating that the lighter varieties of petroleum in the Eastern fields contain nitrogen bases, through the generous kindness of Mr. Orton C. Dunn[5] of Marietta, O., 5 years ago I was able to

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[1] "Mahone Petroleum, Its Origin and the Origin of Petroleum in General," *J. Ind. Eng. Chem.*, 33, 242 (1914); and "The Relations in Chemical Composition of Petroleum to Its Genesis and Geologic Occurrence," *Econ. Geol.*, 1916.

[2] *J. Soc. Chem. Ind.*, 19, 502 (1900).

[3] *Das Erdol*, Leipsic, 1913.

[4] Mabery, *J. Soc. Chem. Ind.*, 18, 504 (1900).

[5] With his scientific education and lifelong connection with the oil and gas industry of this section, there are few men so thoroughly conversant with the geology, manipulation, and technology of the Eastern fields as Mr. Dunn.

procure authentic samples from widely different sections of this territory, and I have since been occupied with the aid of several assistants, a considerable portion of the time in the study of these interesting specimens.

The following table presents the descriptive data of these specimens with those of certain heavier varieties:

TABLE I.

Data of Analyzed Specimens.

Serial number.	Locality.	Rock strata.	Feet in depth.	General data.
1	Dudley, O.	Berea grit	1400	Center of Macksburg Field
2	Emblenton, Pa.	Rosenberg sand	1240	Jane Oil Co., 2nd sand below Berea grit
3	Malto, Ohio	First cow run	38	1000 feet from outcrop. Well 50 yrs. old. 2 bbls. per day
4	Corning, Ohio	Berea grit sand	1150	From J. Denman & Son
5	Marietta, O.	Goose run sand	150	Uppermost producing strata. East of Mississippi River. 200 feet above Pittsburgh coals
6	Newport, Ohio	Berea grit	1170	Eureka field
7	Cabin Creek, W. Virginia	Berea grit	2700	Deepest Berea grit oil sand, running 15 mos.
8	Titusville, Pa.	Third sand	1200	Largest producing sand in Western Pennsylvania
9	Emblenton, Pa.	Third sand	1080	Largest producing sand in Western Pennsylvania
10	Humble Field, Texas, medium	Sand	2750	From Sun Oil Co.
11	Bartlesville, Okla.			
12	Vinton, La.		2750	From Texas Oil Co.
13	Mahone Valley	Pure quartz sand	150	Field flooded by great reservoir
14	Mecca, Ohio	Sand	150	Producing 50 yrs.
15	Sour Lake, Texas	Sand	1300	Sun Oil Co.
16	Beaumont, Texas	Sand	1000	Sun Oil Co.
17	Jennings, La.	Sand	2000	Texas Oil Co.
18	Caddo, La.	Sand	2200	Sun Oil Co.
19	Humble Field, Texas, light		950–1300	Sun Oil Co.
20	Morris, Kansas			
21	Baku, Russia	Sand		Standard Oil Co.

For the detection of the nitrogen bases and determination of nitrogen 3 methods were employed. As a qualitative test one or two liters of the crude oil was vigorously agitated during several hours with dil. hydrochloric acid, the aqueous solution neutralized with sodium hydroxide and extracted with ether. Every specimen examined left on evaporation of the ether, an oily residue with the characteristic odor of the similar bases extracted from California and Russian petroleum in much larger amounts. The smallest yields were observed from the lightest Berea Grit and Pennsylvania crudes, but even these slight residues redissolved in acid and again precipitated with the alkali. Since acids do not remove completely the basic constituents, quantitative results were not possible by this method.

Volumetric Determination of Nitrogen.

On account of the minute amounts of nitrogen in the crude oils, and the difficulty of burning a large weight of the oil, the details of combustion had to be especially adapted and applied with the utmost care. Since the combustion of a gram of the lighter oils gave only a few tenths of a cc. of nitrogen, the preparation of carbon dioxide of sufficient purity, the removal of nitrogen from the copper oxide and the complete combustion of the gases evolved in analysis altogether formed an extremely laborious task. Next to setting up a vacuum-tight apparatus the most tedious detail was the preparation of carbon dioxide sufficiently free from unabsorbable gas and the removal of this gas from the apparatus. Attempts in the beginning to use magnesite failed on account of the large volume of gas needed, and also because magnesite from several different sources contains a considerable proportion of nitrogenous organic matter that decomposes slowly at the temperature at which carbon dioxide is evolved. Sodium hydrogen carbonate and manganous carbonate are so porous it is impossible to expel by heat all the air from the large amount necessary for the desired volume of carbon dioxide. All commercial potassium carbonate contains at least 0.5% of chloride, and chloride-free it costs $2.00 per lb. But after removal of the chloride by silver sulfate, long operation with this carbonate was unsatisfactory in the removal of nitrogen. As a last resort commercial sodium hydrogen carbonate was found to contain only a trace of chloride that is not objectionable, but on account of its porosity, it persistently retains air. In the preparation of a generator, 12 kg. of this carbonate was partly dissolved in 5 liters of boiling water and the boiling continued for some time, then transferred boiling hot to an 8-liter bottle and the boiling continued by vacuum with frequent shaking, until it was cooled to room temperature and the vacuum finally let down with acid. The generator bottle was closed with a rubber stopper twice perforated for a dropping, glass stoppered, sulfuric acid container, and an exit tube, and the neck inclosed in a wide, sheet iron cup which was filled to nearly the top of the neck with plaster of Paris. Within this enclosure which extended above the stopcock of the acid supply was contained sufficient castor oil to seal the stopper and if necessary the stopcock. The sulfuric acid used for generating carbon dioxide was diluted with an equal volume of water which was kept constant while the mixture was boiled for an hour; it was then partly cooled, quickly poured into a separatory funnel under a layer of gasoline and the funnel kept full of carbon dioxide. As the acid was used in the generator the delivery bulb was also kept full of carbon dioxide. The nitrogen was collected in a Schiff nitrometer with a long capillary extension graduated to tenths of a millimeter. A power pump with a gage graduated to millimeters and capable of exhaustion to less than 0.5 mm. was used for obtaining a vacuum, with a large bottle behind it filled with pumice moistened with sulfuric acid to retain moisture. Between this bottle and a full length manometer was an opening for testing the gas and running it off in large amounts.

Complete combustion of the gases evolved in the analysis of petroleum oils as they are mixed with a large proportion of carbon dioxide requires a high temperature and long contact with copper oxide. While a glass tube must be used for the initial decomposition it cannot withstand the final temperature in vacuum operation. Copper oxide slowly fuses into a quartz tube unless a carborundum sleeve is inserted which is inconvenient, and quartz becomes extremely brittle and breaks easily on continued heating especially at very high temperatures. But it is sufficiently durable for a limited number of determinations, and was used for the combustions that were started in vacuum. For a part of those that were made under atmosphere pressure a steel tube was employed with the advantage that temperatures could be maintained up to the fusion of the copper oxide.

The method of analysis was a combination of the Dumas procedure for nitrogen and the oxygen combustion for carbon. In the glass tube in the rear furnace half filled with copper oxide, a vacant space was reserved for the boat containing the oil with an oxidized copper roll close behind it, in the analysis of the lighter oils, and behind that a large boat filled with fused potassium chlorate. In the forward furnace the quartz or steel tube was filled the length of the furnace with coarse wire copper oxide and the projecting ends were kept cold. Tight joints at the ends of both tubes were maintained with seals of castor oil over rubber stoppers. Other connections were made vacuum tight by means of a special form of thick rubber tube with narrow bore, obtained from the Nela Park laboratory of the General Electric Company, also luted with castor oil.

With all connections of the apparatus properly adjusted the next step was the removal of air which included the film adhering to the entire inner surface, the adsorbed gas from the copper oxide, and most difficult of all that persistently held by the solid hydrogen carbonate. Then with the temperature of the copper oxide in the glass tube held as high as the tube would stand, and in the silica tube at full red heat, the system was repeatedly evacuated and filled with carbon dioxide extending through several days, until tests showed that the unabsorbable gas was removed to the limit of at least one part in 30,000, and combustion of one g. of sugar gave 0.1 cc. of gas not absorbed, when part of the analyses were made, and 0.05 cc. at other times, which were the corrections applied to the specimens of oil analyzed. Continuous operation of the apparatus for two weeks until the supply of bicarbonate in the generator was completely exhausted failed to reduce the amount of unabsorbable gas lower than this limit. Since the nitrogen bases in petroleum are not volatile in air or in vacuum at ordinary temperatures in the analysis of the lighter oils much time was saved by allowing the more volatile hydrocarbons to evaporate in the air to the extent of $^1/_3$ or more of the weight of the oil, and complete combustion of these oils was more readily assured by beginning the analysis under vacuum. Since nitrogen is always held by the residual coke this must be completely burned in a stream of oxygen from the rear potassium chlorate; a slow evolution of oxygen from the

TABLE II.

Percentages of Nitrogen in Specimens of Table I.

Serial number.	Sp. gr.	Total wt. of oil.	Cc. of nitrogen.	Correction.	No. cc. in oil.	% nitrogen in oil.	% by Kjeldahl.
1	0.8238	0.6475	0.25	0.09	0.16	0.027	0.022
2	0.8809	0.7890	0.21	0.09	0.1	0.0136	0.014
3	0.8326	0.8707	0.41	0.09	0.32	0.039	0.043
4	0.8404	0.9205	0.45	0.09	0.36	0.41	0.045
5	0.7907	0.9865	0.24	0.09	0.15	0.016	0.019
6	0.7904	1.0876	0.33	0.09	0.24	0.024	0.014
7	0.8139	1.0732	0.39	0.09	0.30	0.029	0.049
8	0.7904	0.7525	0.22	0.09	0.13	0.018	0.01
	..	1.2445	0.15	0.05	0.10	0.01	...
9	0.8007	0.8913	0.19	0.09	0.1	0.012	0.011
	..	1.7550	0.20	0.05	0.15	0.011	...
10	0.9066	0.7535	0.54	0.09	0.45	0.058	0.068
11	0.8625	0.6458	0.58	0.09	0.48	0.074	0.082
12	0.9014	0.6854	0.55	0.09	0.46	0.067	0.079
13	0.9036	0.9023	0.40	0.05	0.35	0.049	0.054
14	0.9023	0.7020	0.35	0.05	0.30	0.054	0.044
15	0.9302	0.8218	0.64	0.09	0.55	0.067	0.082
16	0.9175	0.5630	0.25	0.09	0.16	0.023	0.016
17	0.9054	0.6220	0.39	0.09	0.30	0.48	0.039
18	0.8584	0.6000	0.39	0.09	0.30	0.050	0.057
19	0.8227	1.9985	0.39	0.09	0.30	0.015	0.017
20	0.8499	0.9870	0.44	0.09	0.35	0.035	0.045
21	0.8650	0.7021	0.45	0.05	0.40	0.071	0.06
Coke (No. 7) from 1000 g. oil, 70 g. coke		1.6501	1.8	0.09	1.76	0.13	...
Nitrogen from oil retained in coke						0.009	...

beginning of the combustion without the aid of the copper roll is sufficient to prevent backward distillation, and it aids the forward movement and partial burning of the gases. After the oil is completely burned the tubes are swept clear of nitrogen with carbon dioxide from the generator, and the reduced copper oxide reoxidized with tank oxygen. If this be done with the tubes hot, after a few evacuations the system is ready for the next analysis. Even with this large surface of copper oxide the combustion cannot be pushed too rapidly for unburned gases will escape. One g. of oil requires two to three hours in safe operation. The average room temperature, 25°, and the average barometer readings 740 mm. were used in the reduction of the volume of nitrogen to standard conditions. In the preceding table are presented the data of the volumetric determinations together with analysis of the same specimens by the Kjeldahl method using 5 g. of the oil, which were made by Professor M. F. Coolbaugh.

Summary.

Proof has been given of the presence of nitrogen in petroleum of all the principal oil fields, in forms of combination that could have had their origin only in the remains of vegetable or animal bodies. Presumptive evidence has been shown that the associated hydrocarbons in petroleum had the same origin.

A special method of analysis for the determination of minute proportions of nitrogen in oils is described.

CLEVELAND, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

STUDIES IN THE CYCLOPROPANE SERIES. IX. NITROCYCLOPROPANE DERIVATIVES.

BY ELMER PETER KOHLER AND M. SRINIVASA RAO.

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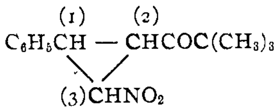
The following paper deals with a cyclopropane derivative which has an alkyl group in place of one of the aryl groups contained in all the nitrocyclopropane derivatives described in earlier papers. Substances of this type are not easily made. In order to avoid complications in preparation it finally proved necessary to use tertiary butyl compounds. The substance studied, therefore, was phenyl-trimethylacetyl-nitrocyclopropane:



This substance was made without much difficulty by adding nitromethane to benzalpinacoline, brominating the addition product, and eliminating hydrogen bromide from the resulting bromo compound: