TABLE I

2-SUBSTITUTED THIOPHENES AND DERIVATIVES[a]

	Yield, %	B. p., °C. (1 mm.)	$d^{20}{}_4$[b]	$n^{20}{}_D$	Formula	Sulfur, % Calcd.	Sulfur, % Found	Oximes M. p., °C.	Oximes Sulfur, % Calcd.	Oximes Sulfur, % Found
2-Hexanoylthiophene[c]	78	117–119	1.065	1.5301	$C_{10}H_{14}OS$	17.59	17.73	53–54[d]	16.25	16.58
2-Octanoylthiophene[e]	78	140–143	1.005	1.5214	$C_{12}H_{18}OS$	15.24	14.88	56–57[f]	14.23	14.30
2-Nonanoylthiophene[g]	80	155–157	0.970	1.4917	$C_{13}H_{20}OS$	14.29	13.85	(Oil)[h]		
1-(2-thienyl)-hexanol	60	110–112	1.055	1.5155	$C_{10}H_{16}OS$	17.40	17.48			
1-(2-thienyl)-octanol	41	133–135	0.973	1.5203	$C_{12}H_{20}OS$	15.10	15.37			
1-(2-thienyl)-nonanol	47	149–152	.938	1.4902	$C_{13}H_{22}OS$	13.45	13.71			
								5-Chloromercuri-	Mercury, % Calcd.	Found
2-Hexylthiophene	44	79–82	.946	1.4970	$C_{10}H_{16}S$	19.05	19.02	140–141[i]	49.8	49.3
2-Octylthiophene[j]	55	106–108	.920	1.4824	$C_{12}H_{20}S$	16.33	15.94	136–137[i]	46.5	46.3
2-Nonylthiophene	38	128–131	.906	1.4763	$C_{13}H_{22}S$	15.24	15.11	135–136[i]	45.0	44.6

[a] All boiling and melting points uncorrected. [b] All density measurements made with a Fisher–Davidson Gravitometer. [c] Semicarbazone, m. p. 133–134°; % S, calcd.,13.40; found, 13.59. 2,4-DNP (2,4-dinitrophenylhydrazone), m. p. 152–153°; % S, calcd., 8.85; found, 9.10. [d] Yield, 83% on 0.1 mole run. [e] Semicarbazone, m. p. 127–129°; % S, calcd., 11.99; found, 12.27. 2,4-DNP, m. p. 123–125; % S, calcd., 8.21; found, 8.40. [f] Mixed m. p. with 2-hexanoylthiophene oxime, 48–51°. [g] Semicarbazone, m. p. 134–135 (mixed m. p. with 2-hexanoylthiophene semicarbazone, 103–109°). % S, calcd., 11.40; found, 11.50. 2,4-DNP, m. p. 108–109°. % S, calcd., 7.93; found, 7.73. [h] An intractable oil, not isolated. [i] Mixture of all possible pairs of these three derivatives melted about 40° lower and over a 20° range, *i. e.*, about 95–120°. [j] Prepared by Schweinitz (*Ber.*, 19, 644 (1886)) by a Wurtz–Fittig reaction, b. p. 257–259°.

added to the reaction mixture and distillation continued until 25 ml. of distillate had been collected. The residue was decomposed with dilute acid, extracted with ether and the ether extracts washed and dried over potassium carbonate. Distillation of the ether-free residue yielded 2.8 g. (47%) of 1-(2-thienyl)-nonanol, b.p. 150–156° at 2 mm.

Acknowledgment.—We are deeply indebted to the Ohio Oil Company for the financial support of this research.

Summary

A number of thiophenes having alkyl, 1-alkanol and acyl groups substituted in the 2-position have been synthesized and characterized. Some solid derivatives of these compounds have also been made.

BLOOMINGTON, INDIANA RECEIVED AUGUST 15, 1947

[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY, THE PENNSYLVANIA STATE COLLEGE]

The Distribution of Nitrogen in the Oxidation Products of Coals and Selected Nitrogen Compounds[1]

BY C. R. KINNEY, J. W. ECKERD, PAULINE REXFORD AND H. B. CHARMBURY

The chemical nature of the nitrogen occurring in coals is little understood, although it is agreed that its source is the proteins of the plants, animals, and microörganisms that inhabited the coal-swamps. In a peat, as much as 78.5% of the nitrogen can be extracted by dilute acid[2] but the percentage of the nitrogen extracted from coals rapidly falls with increasing rank; lignite, 21.8%; bituminous coal, 5.4%; anthracite, 2.6%. The nitrogen compounds which are extracted are largely amino acids among which present-day acids have been identified. The decrease in extractability of nitrogen compounds from the higher rank fuels indicates that the proteins or the amino acids present in the original starting material have undergone condensation reactions, possibly of the type suggested by Maillard.[3]

A knowledge of the chemical nature of the nitrogen in coal might be of particular value in the coking industry because of the possibility of making changes in the yields of nitrogen products and it might also be of importance in the hydrogenation of coal because of the amines which may be obtained. When coal is coked, 50% or more of the nitrogen remains in the coke,[4,5] about 15–20% is evolved as ammonia and 25–30% as free nitrogen. The formation of a variety of nitrogen-containing products strongly suggests that more than one nitrogen structure occurs in coal.

On the hydrogenolysis of coal[6] a considerable part of the nitrogen is evolved as ammonia. At moderate temperatures, less than 500°, the maxi-

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[1] Presented before the Division of Gas and Fuels, Atlantic City Meeting of the American Chemical Society, April 17, 1947.

[2] Shacklock and Drakely, *J. Soc. Chem. Ind.*, **46**, 478–81T (1927).

[3] Maillard, *Ann. chim.*, **7**, 113–152 (1917); for a discussion of this work see "Chemistry of Coal Utilization," H. H. Lowry, Editor, John Wiley and Sons, Inc., New York, N. Y., 1945, chapter 13, W. R. Kirner, page 452.

[4] In the older literature low nitrogen analyses of cokes were reported because the ordinary Kjeldahl procedure failed to obtain all of the nitrogen from cokes and to obtain a material balance the difference was often ascribed to a larger yield of gaseous nitrogen.

[5] Lowry, Landan and Naugle, *Trans. A. I. M. E.*, **149**, 297–330 (1942), have published average percentages of nitrogen distributed among the carbonization products of a number of coals. Using these data it can be calculated that the average per cent. of the nitrogen remaining in 1000°-coke is 56.6%.

[6] Storch, Hirst, Fisher and Sprunk, *U. S. Bur. Mines Tech. Paper* **622**, 53, Table 24 (1941).

TABLE I

PERCENTAGE DISTRIBUTION OF NITROGEN IN THE OXIDATION PRODUCTS OF COAL[a]

Coals	N in coal, Kjeldahl	Total N, oxid.	Difference in Kjeldahl and oxidation N	N from coal as NH_3	N from coal as NO_3^-	Proportion of N as NH_3	Proportion of N as NO_3^-
Lignite, Velva, No. Dakota	0.85	0.74	−0.11	0.46	0.28	61.6	38.4
Sub-bituminous, Monarch, Wyoming	1.51	1.31	.20	.80	.51	61.3	38.7
Bituminous, high-volatile A							
Upper Freeport, Pennsylvania	1.38	1.34	.04	.88	.46	65.9	34.1
Pittsburgh, Pennsylvania	1.66	1.35	.31	.88	.47	65.2	34.8
No. 2, Washington,	2.11	1.92	.19	1.34	.58	69.9	30.1
Medium-volatile Sewell, West Virginia,	1.68	1.32	.36	0.86	.46	65.4	34.6
Low-volatile Pocahontas No. 3, West Virginia	1.24	1.04	.20	.66	.38	63.7	36.3
Anthracite, high-volatile, Williamstown, Pa.	0.95	1.02	+ .07	.67	.35	65.3	34.7
Low-volatile, Highland, Pa.	.82	0.77	− .05	.42	.35	54.8	45.2
Coke, metallurgical, from							
Pittsburgh Bed Coal above	1.12	.36	.76	.13	.23	36.1	63.9
Breeze from same	0.77	.58	.22	.34	.24	58.7	41.3

[a] As received basis. All samples were minus 60 mesh. Metallurgical coke 95% minus 150 mesh; coke breeze 90% minus 100 mesh.

mum amount of ammonia appears to be about 30–35%. The remainder of the nitrogen is converted to nitrogen containing oils, which are probably amines. This also suggests that coals contain more than one kind of nitrogen structure. On the other hand Fisher and Eisner[7] have shown that the rate of removal of nitrogen during hydrogenolysis of coal is constant although quite slow, at least over the temperature range of 385–415° and up to twelve hours time. This may be due to the presence of only one form of nitrogen in coal but it seems more reasonable to assume that the constant rate of nitrogen removal is dependent upon another reaction which is relatively slow.

In view of these differences in the behavior of nitrogen in coals, an investigation of the distribution of the nitrogen in the products of the oxidation of coals and of a variety of pure organic compounds has been made. As the oxidizing reagent for this purpose, alkaline permanganate was selected.

Experimental

Oxidation Procedure.—Oxidations were carried out in iron kettles of 3 liters capacity, equipped with condensers of one meter length and with an opening for admitting air. Samples of 3 g. were used with 60 g. of potassium permanganate and 50 g. of potassium hydroxide dissolved in a liter of water. The mixture was refluxed and any ammonia that was formed was carried out by a slow stream of air entering the kettle, passing out through the condenser and into a beaker containing standard acid. A plug of glass wool was inserted in the top of the condenser to prevent any spray from being carried into the acid. The oxidation was continued until only traces of ammonia (less than 0.01% nitrogen) were obtained in an eight hour period of refluxing. The residue was then tested quantitatively for nitrate ion.

The Determination of Ammonia.—The ammonia formed during the oxidation was trapped in 400-ml. tall-form beakers containing 25 ml. of 0.1 *N* sulfuric acid diluted to 200 ml. With most of the samples used several days of refluxing were required to complete the liberation of ammonia and in these cases a fresh lot of acid was used daily. The amount of ammonia was determined by back titration with 0.1 *N* base using methyl red indicator. When the ammonia titration fell below 0.01% nitrogen in the sample on two successive days, the liberation of ammonia was considered to be complete.

Since ammonia might be oxidized by alkaline permanganate, test runs were made with samples of ammonium chloride. The per cent. nitrogen obtained was 26.22 and 26.32% which compared with the theory of 26.17% shows that ammonia is not readily oxidized by alkaline permanganate.

The Determination of Nitrate Nitrogen.—After the ammonia had been completely removed, the excess permanganate was destroyed with formic acid. The manganese dioxide was filtered out and washed thoroughly. The filtrate and washings were returned to the kettle together with 50 g. of potassium hydroxide and 20 g. of Devarda alloy. The condenser and air inlet were arranged as before to collect the ammonia formed by the reduction of the nitrate ion. When all of the alloy had reacted, the ammonia was distilled out and titrated in the usual manner.

The results of these determinations, calculated as per cent. of nitrogen in the sample, are arranged in Tables I and II.

Discussion

Table I gives the data obtained from the various coals and cokes oxidized. The total quantity of nitrogen recovered during the oxidation approached that obtained by the Kjeldahl procedure. The difference between the two results varied between −0.36 and ±0.07% nitrogen in the sample. Similar differences between the theory and the total recovered nitrogen from the pure compounds (Table II) were observed and it seems likely that certain nitrogen structures are not quantitatively partitioned into ammonia and nitrate. Possibly, in these cases, a part of the nitrogen is converted into free nitrogen since it escapes detection.

Also in Table I are compared the percentages of nitrogen converted to ammonia and nitrate ion and the relative percentages of ammonia and nitrate based on the total of these products. It will be observed that about two-thirds of the nitrogen is liberated as ammonia from the coal samples,

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(7) Fisher and Eisner, *Ind. Eng. Chem.*, **29**, 1371 (1937).

TABLE II

PERCENTAGE DISTRIBUTION OF NITROGEN IN THE OXIDATION PRODUCTS OF CERTAIN ORGANIC SUBSTANCES

Substance	Oxid. hours	Total N	N as NH_3	N as NO_3^-	Proportion of N as NH_3	Proportion of N as NO_3^-
Glycine[a]	75	99.8	99.8	..	100.0	0.0
Nicotinic acid[a]	76	95.8	95.8[b]	..	95.8	..
p-Aminobenzoic acid[a]	43	72.0	54.7	17.3	76.0	24.0
p-Benzalaminophenol	75	98.0	71.7	26.3	73.2	26.8
β-Naphthylamine	107	87.7	56.3	31.4	64.2	35.8
Diethanolamine	63	85.4	52.7	32.7	61.7	38.3
Carbazole	255	87.4	50.6	36.8	57.9	42.1
Diphenylamine	120	81.0	42.9	38.1	53.0	47.0
Edestin	107	96.7	57.9	38.8	59.8	40.2
Gluten (wheat)	117	91.0	50.8	40.2	55.8	44.2
Benzalaniline	79	94.9	39.7	55.2	41.8	58.2
p-Nitrobenzoic acid[a]	28	93.1	3.3	89.8	3.5	96.5

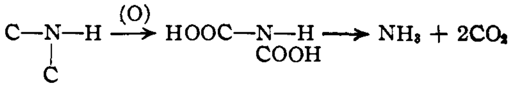
[a] Glass apparatus used. [b] Flask destroyed by the alkali at this point.

with the exception of the low-volatile anthracite, and about one-third as nitrate. With the low-volatile anthracite and the coke samples, a larger yield of nitrate was obtained and less ammonia.

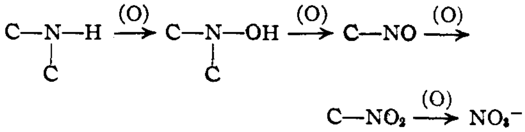
These results most closely approximate the yields of ammonia and nitrate ion obtained from β-naphthylamine (Table II). The secondary amine structure in diethanolamine, carbazole and diphenylamine also appears to be a possibility, particularly if other structures are present to offset the somewhat low yield of ammonia. The imino grouping in *p*-benzalaminophenol and benzalaniline gave more widely separated results, but apparently this structure is also a possibility depending upon the character of other groups in combination with it.

The results obtained with the plant proteins, edestin and wheat gluten, suggest that, while proteins are not present in coal, the basic nitrogen structures in the proteins have not been greatly altered by the process of coalification. Because of the almost quantitative yields of ammonia from glycine and nicotinic acid, structures such as these would be expected to be present in coal in relatively small quantities. For the same reason the nitro group which is oxidized in high yield to nitrate would not be expected in coal.

The mechanism of the oxidation of nitrogen-containing carbon compounds with the liberation of nitrogen as ammonia seems most likely to be the result of reaction (1) while the oxidation of nitrogen to nitrate ion may be accounted for by reaction (2).

(1)


$$\text{C—}\underset{\substack{|\\ \text{C}}}{\text{N}}\text{—H} \xrightarrow{(\text{O})} \text{HOOC—}\underset{\text{COOH}}{\text{N}}\text{—H} \longrightarrow NH_3 + 2CO_2$$

(2)


$$\text{C—}\underset{\substack{|\\ \text{C}}}{\text{N}}\text{—H} \xrightarrow{(\text{O})} \text{C—}\underset{\substack{|\\ \text{C}}}{\text{N}}\text{—OH} \xrightarrow{(\text{O})} \text{C—NO} \xrightarrow{(\text{O})} \text{C—}NO_2 \xrightarrow{(\text{O})} NO_3^-$$

From the results in Table II it would appear that the two reactions are competitive, but that in those compounds in which a higher oxidation potential is required to oxidize the carbon radical a greater proportion of the nitrogen is oxidized to nitrate.[8]

While alkaline permanganate does not differentiate sharply between all of the various nitrogen structures, the surprising constancy of the quantities of ammonia and nitrate obtained from the various ranks of coal, considering the wide variations in yields from pure compounds, indicate that coals of different rank and from different localities contain the same kind of nitrogen linkages, that these similar nitrogen structures were produced in all coals by means of similar chemical reactions acting on similar proteins which were present in the peats from which the coals were made and that on oxidation these structures gave about the same yields of ammonia and nitrate ion. These condensed structures, formed during coalification, may possibly be aromatic amino or imino derivatives related to those in Table II, although an essentially carbon structure in which the carbon atoms are interspersed with nitrogen atoms appears likely for the cokes and possibly to a limited extent in anthracites and the fusain and opaque attritus of the lower rank coals as well. Such a structure would be, so far as the nitrogen is concerned, that of a tertiary amine. This conclusion is suggested by the higher yield of nitrate ion obtained from cokes and low volatile anthracite.

Summary

The oxidation of coals with alkaline permanganate liberates the nitrogen in two forms, ammonia and nitrate ion. A comparison of the relative amounts with similar data obtained from pure nitrogen compounds has been made.

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[8] In this connection, a less vigorous oxidizing reagent than alkaline permanganate might better differentiate between certain nitrogen structures.