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THE SEPARATION AND STRUCTURE ELUCIDATION OF COAL MOLECULE FRAGMENTS

Final Report, February 1, 1976—August 31, 1979

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January 1980

Work Performed Under Contract No. EY-76-S-02-2856

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ABSTRACT

Separation and identification of the polynuclear aromatic and aliphatic fractions of solvent-refined coal and its recycle oil were performed using a combination of solvent partition and chromatographic fractionation procedures with glass-capillary gas chromatography/mass spectrometry. Chromatographic profiles were generated for each fraction and some semiquantitative data were also obtained. In total, 146 polynuclear aromatic components of SRC were tentatively identified by their molecular weights, as indicated by the mass spectra of the gas chromatography peaks. In addition, whereever possible, specific isomers have been indicated, based on comparison of spectral characteristics and retention data.

Separation and identification of nitrogen-containing aromatics of the recycle oil of SRC was accomplished with a combination solvent partition and capillary gas chromatography with deactivated glass columns. High-precision retention measurements of known pyridine and quinoline derivatives are reported, utilizing parent aza-arenes as retention standards. Both precisely measured retention data and mass spectral information combined lead to positive identification of some compounds in SRC samples. A total of 48 two-membered or three-membered aza-arenes have been tentatively identified in the recycle oil.

Gas Chromatography-Mass Spectrometric Determination of Nitrogen Aromatic Compounds in SRC Recycle Oil

INTRODUCTION

Occurrence of nitrogen-containing polyaromatic compounds (so-called aza-arenes) in various fuels and products of combustion is well-established. Their structural elucidation and reliable quantitative analysis in such mixtures will be required for improved understanding of the mechanism by which such compounds are formed as well as to assess a potential environmental hazard.

While earlier studies pointed out (1) that certain aza-arenes can be even more potent carcinogens than the most active neutral polyaromatic hydrocarbons, more recent results of biological testing with fossil fuels (2) and other environmental mixtures (3) further reinforce their importance.

Whereas the methodology for separation and identification of neutral polycyclic aromatic hydrocarbons is becoming fairly well-established, only few analytical studies are reported with aza-arene mixtures. This reflects, in major part, difficulties generally encountered with efficient chromatography of nitrogen-containing compounds. In order to provide methodology comparable with the recently advanced analytical methods for neutral polyaromatics (4-7), studies have been undertaken in this laboratory to develop glass capillary column techniques for nitrogen aromatics.

While recognizing the fact that peak symmetry and minimum residual activity of glass columns are important for both

effective component resolution and quantitation, deactivation with surface-active compounds was optimized. The volatility range with the present study extends up to tricyclic compounds.

Due to the complexity of various nitrogen-containing mixtures and the natural occurrence of many isomers, identification ideally requires a maximum utilization of both chromatographic and spectroscopic techniques. This has also been demonstrated with neutral polyaromatics, where accurately measured retention data (7) together with special mass-spectroscopic techniques (8) can provide positive identifications of many closely related isomers.

In accordance with our previous work (7) on normal polyaromatics, exact determinations of various substituted pyridine and quinoline derivatives were carried out using the "homologous" series of pyridine, quinoline, and acridine. This information was essential in assigning structures to certain peaks within the complex mixtures from coal-derived materials. Many additional alkylated isomeric components were identified from their differences in mass-spectral intensities, as suggested by Draper and MacLean (9,10).

The utilization of capillary gas chromatography/mass spectrometry (GC/MS) in the analysis of nitrogen aromatics is demonstrated in this work with the recycle oil of solvent-refined coal (SRC). Interest in coal as an organic feedstock as well as its conversion to liquid fuels has now prompted numerous attempts to improve our understanding of its chemical composition. Although the "bulk" methods (e.g., elemental

analyses, vapor pressure osmometry, and nuclear magnetic resonance) are recognized to provide some important information (11,12) related to heat content, different methodologies must be utilized to provide identification of the individual components.

EXPERIMENTAL

Capillary Gas Chromatography and Combined GC/MS

Varian Model 1400 gas chromatography modified for work with glass capillary columns was used for most chromatographic measurements, including those of retention values for substituted pyridines and quinolines. A modified Perkin-Elmer 3920 gas chromatograph and PEP-2 data acquisition system were employed in recording quantitatively the nitrogen compound profiles originated from the SRC recycle oil. While both gas chromatographs were equipped with a splitless injection system, the Perkin-Elmer instrument was further provided with the flame photometric (sulfur-sensitive) and thermionic (nitrogen-sensitive) detectors assembled in parallel with the flame ionization detector.

Glass capillary columns were prepared from the soft glass tubing material, drawn to 0.25 mm, i.d. Glass capillaries were "etched" (13) with gaseous HCl at 400°C and statically coated with UCON 50-HB-2000 stationary phase. Kalignost (tetraphenylboron sodium) or BTPPC ([benzyl]triphenylphosphonium chloride), both products of Aldrich Chemicals, Inc., are added directly to the stationary-phase solution, in order to form a 10% addition to the amount of the polymer phase used. They provide the necessary deactivation (14) for an effective chromatography of numerous nitrogen compounds.

Sample introduction was accomplished by direct syringe

injection, or placement of the sample onto a deactivated precolumn (15), with a subsequent removal of solvent with purified helium at room temperature. After the precolumn is placed into the heated injector (210°C), the sample is re-trapped at the head of the analytical column held at room temperature. The capillary column was programmed from 50 to 180°C at 2°C/min. Various pyridine and quinoline derivatives were injected at 15 ng per component in 0.2 μl methylene chloride for the retention studies.

Mass-spectral data were obtained with a Hewlett-Packard 5980A combined gas chromatograph/mass spectrometer. Glass capillary columns were connected directly to the ion source of the dodecapole mass spectrometer. The instrument was calibrated with perfluorotributylamine and electron impact spectra were recorded at the ionization energy of 70 eV. Mass spectra were compared with those previously recorded and conformational isomers were further judged by retention of available standards.

Coal Sample Preparation

The samples of SRC recycle oil used in these studies were obtained from the Pittsburgh and Midway Mining Company, Dupont, Washington. All solvents used were of spectral grade (Fisher Scientific Company, Fairlawn, New Jersey) and were redistilled whenever necessary prior to use. Water was redistilled from $KMnO_4$/KOH to remove organic material and reduce blanks.

Solvent partition of the SRC recycle oil sample was carried out following the method of Novotny et al. (4). 10.5 g of recycle oil per 250 ml of methylene chloride was used. Yields of the specific fractions have already been reported (16).

RESULTS AND DISCUSSION

It is generally appreciated that gas chromatography of nitrogen-containing compounds can often be a difficult task. The difficulties are directly attributable to the column irreversible adsorption phenomena and peak asymmetry. They are particularly pronounced in capillary GC due to the smaller sizes of analyzed samples. While generally applicable approaches to deactivation of glass capillary columns (17,18) are of relatively recent date, it is demonstrated here that simple addition of a surface-active substance to the stationary phase can largely avoid the tailing problem with bases. Column-to-column reproducibility of this phenomenon is very good.

While combined GC/MS is a powerful method in general, it is difficult to assign positively structures to various isomers within the mixtures of nitrogen compounds as based on mass-spectral information alone. Recently, we have shown (7) that precisely measured and suitabley referenced retention data can significantly aid in positive identification of conventional polycyclic aromatic hydrocarbons. When a series of parent polyaromatics are used as retention reference compounds, comparisons among individually prepared glass capillary columns within one laboratory as well as different laboratories become feasible. This concept is extended here to various isomeric nitrogen compounds.

In order to reference various pyridine and quinoline derivatives (or other nitrogen compounds within a given volatility range), a series of retention standards was chosen consisting of pyridine, quinoline and acridine. While n-alkanes or even neutral polyaromatics were found unreliable as reference retention standards for the nitrogen aromatic bases, a high degree of reproducibility has been achieved using the aza-arene standards. Table 1 lists a number of alkylated bases together with their "retention indices" (as referenced to I-values equal to 100, 200, and 300, for pyridine, quinoline, and acridine, respectively). All values are an average of 5 measurements, with a standard deviation of no more than 0.3 retention units and typically around 0.15 units. With the great precision of such measurements and due to the high resolving power of glass capillary columns, many conformational isomers can safely be identified.

The applicability of the fractionation scheme reported earlier (4,16) to isolate nitrogen-containing compounds from a complex mixture has been indicated. While using our three detector parallel assembly, specificity of this fractionation has been ascertained through a peak-by-peak agreement between the flame ionization and the nitrogen-sensitive detectors; no sulfur components were revealed in this fraction.

A chromatographic profile of the basic fraction of SRC recycle oil was obtained. The components identified by GC/MS are numbered and listed in Table II, which also includes semiquantitative data on identified components. Equal weight

responses were assumed for all concerned components.

In total, 41 compounds were tentatively identified through their mass spectra. In eight additional cases of alkylated isomers, mass spectra and retention values of authentic compounds were found to coincide with the mixture components. The bases in this sample range from two-membered to three-membered rings. The absence of pyridine derivatives is understandable, since the high-volatility materials were removed from the recycle oil through distillation.

Two types of compounds seem predominant in the studies sample: (a) alkylated quinolines (or isoquinolines); and, (b) alkyl-substituted phenyl pyridines, or aza-acenaphthenes, or cyclopentaquinolines. The latter type of compounds is favored due to the simple fragmentation pattern of the aromatic fused rings. If the structures were alkylated phenyl pyridines, a strong peak at m/e 77 should be observed.

In confirming the individual structures of alkylated quinolines, mass-spectral data can be informative. Draper and MacLean (9) have shown that the parent ion forms the base peak for dialkylquinolines if the alkyl group is methyl. They also postulated the reason for this observation (10). As found in this work (Table III), the same rule applies for the mass spectra of trimethylated and tetramethylated quinolines. Thus, wherever the parent ion was not the base peak, the solely substituted methyl isomer could be ruled out. Wherever the parent ion formed the base peak, the structure of a fully methylated isomer could be assigned.

While identification of the remaining constituents of SRC will primarily need acquisition of additional standards, this work demonstrates feasibility of the described analytical approach. Adequate glass capillary column technology is now available for studying basic components within the described volatility range. However, high-efficiency separations of heavier aza-arenes need further attention.

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TABLE I

"Retention indices" of alkylated pyridines, quinolines, and related compounds

(A) Column: 50 m x 0.25 mm, i.d., glass capillary column coated statically with UCON 50-HB-2000 and Kalignost.

Compound	Average index value	Standard deviation
2-methylpyridine	106.48	0.11
2-methylpyrazine	111.04	0.16
2,6-dimethylpyridine	113.75	0.17
3-methylpyridine	115.49	0.24
4-methylpyridine	116.26	0.20
2-ethylpyridine	117.65	0.21
2,5-dimethylpyridine	123.36	0.23
2,4-dimethylpyridine	124.64	0.21
2,3-dimethylpyridine	127.35	0.22
3-ethylpyridine	130.17	0.25
4-ethylpyridine	131.76	0.24
2,4,6-trimethylpyridine	132.89	0.25
3,4-dimethylpyridine	141.96	0.22
4-vinylpyridine	142.77	0.23
2(3-pentyl)pyridine	146.68	0.22
4-t-butylpyridine	151.59	0.20
3-ethyl-4-methylpyridine	155.36	0.21
2-aminopyridine	192.62	0.06
2-amino-6-methylpyridine	197.81	0.32

Table I (continued)

(B) Column: 20 m x 0.25 mm, i.d., glass capillary column coated statically with UCON 50-HB-2000 and BTPPC.

Compound	Average index value	Standard deviation
8-methylquinoline	207.25	0.10
2-methylquinoline	207.88	0.11
2,8-dimethylquinoline	211.86	0.09
8-ethylquinoline	216.86	0.05
6-methylquinoline	218.00	0.20
3-methylquinoline	218.53	0.14
2-isopropylquinoline	220.54	0.17
4-methylquinoline	223.76	0.12
6,8-dimethylquinoline	224.74	0.09
2,7-dimethylquinoline	225.21	0.08
8-n-propylquinoline	228.72	0.04
2,6,8-trimethylquinoline	228.75	0.08
4,8-dimethylquinoline	230.04	0.16
2-n-propylquinoline	230.98	0.09
2,4-dimethylquinoline	231.06	0.13
2,3-dimethylquinoline	231.54	0.08
3-ethylquinoline	232.62	0.14
6-ethylquinoline	232.65	0.10
2,4,8-trimethylquinoline	233.98	0.09
2-ethyl-3-methylquinoline	238.34	0.16
2-ethyl-3-methylquinoline	238.35	0.14
6,7-dimethylquinoline	243.59	0.20
3,5,8-trimethylquinoline	245.41	0.06
6-n-propylquinoline	245.82	0.07
5,6-dimethylquinoline	246.53	0.13
4-n-propylquinoline	246.90	0.10
2,4,6-trimethylquinoline	247.39	0.09
2,4,7-trimethylquinoline	247.50	0.08
3,4-dimethylquinoline	248.70	0.12

Table I (continued)

Compound	Average index value	Standard deviation
2,4-diethylquinoline	249.09	0.05
2,4,6,8-tetramethylquinoline	249.50	0.13
2,6,7-trimethylquinoline	249.88	0.11
3-methyl,4-ethylquinoline	253.73	0.11
3,7-dimethylquinoline	254.36	0.12
2-ethyl-3,5-dimethylquinoline	257.45	0.06
2-ethyl-3,5,8-trimethylquinoline	260.21	0.04
2,3,4-trimethylquinoline	260.61	0.08
3,4,7-trimethylquinoline	264.91	0.04
3,6-dimethyl-4-ethylquinoline	267.30	0.09
2,4,6,7-tetramethylquinoline	270.29	0.08
3,4,5,8-tetramethylquinoline	279.49	0.04
3,4,6,7-tetramethylquinoline	287.64	0.12
2,3,4,6,7-pentamethylquinoline	297.23	0.11

TABLE II

Identified and Possible Basic Components of SRC Recycle Oil

Peak #	Molecular Weight	Formula	Concentration Parts-per-thousand in the basic fraction	Concentration Parts-per-million in SRC oil	Compound Name
1	143	$C_{10}H_9N$	0.23	4.0	[a] 2-methylquinoline
2	161	$C_{11}H_{15}N$	0.23	4.0	me^2- or ethyltetrahydroquinoline/isoquinoline
3	143	$C_{10}H_9N$	0.30	5.2	[a] 6-methylquinoline
4	143	$C_{10}H_9N$	0.35	6.1	[a] 3-methylquinoline
5	157	$C_{11}H_{11}N$	1.26	21.9	[a] 2,6-me^2-quinoline
6	175	$C_{12}H_{17}N$	0.38	6.6	me^3- or ethyl-methyl, or propyl-tetrahydroquinoline/isoquinoline
7	175	$C_{12}H_{17}N$	1.47	25.5	me^3- or ethyl-methyl, or propyl-tetrahydroquinoline/isoquinoline
8	157	$C_{11}H_{11}N$	0.07	1.2	me^2-quinoline/isoquinoline
9	143	$C_{10}H_9N$	0.04	0.7	me^2-quinoline/isoquinoline
10	157	$C_{11}H_{11}N$	0.28	4.8	[a] 2,3-dimethylquinoline
11	157	$C_{11}H_{11}N$	1.29	22.4	[a],[b] 3-ethylquinoline
12	157	$C_{11}H_{11}N$	0.34	5.9	ethylquinoline
13	157	$C_{11}H_{11}N$	1.50	26.0	me^2-quinoline/isoquinoline isomer
14	171	$C_{12}H_{13}N$	1.57	27.3	ethyl-methyl-, or propyl-quinoline/isoquinoline
15	157	$C_{11}H_{11}N$	0.22	3.8	ethylquinoline/isoquinoline
16	185	$C_{13}H_{15}N$	0.55	9.5	propyl-methyl, or butyl, or et^2-quinoline/isoquinoline

Table II (continued)

Peak #	Molecular Weight	Formula	Concentration Parts-per-thousand in the basic fraction	Concentration Parts-per million in SRC oil	Compound Name
17	171	$C_{12}H_{13}N$	0.41	7.1	propyl, or ethyl-methylquinoline/ isoquinoline
18	189	$C_{13}H_{19}N$	0.33	5.7	me^4- or et^2- or propylmethyl, or butyl, or me^2-ethyltetrahydroquinoline/ isoquinoline
19	171	$C_{12}H_{13}N$	1.44	25.0	ethyl-methyl, or propylquinoline/ isoquinoline
20	171	$C_{12}H_{13}N$	0.47	8.1	[a] 4-n-propylquinoline
21	171	$C_{12}H_{13}N$	3.47	60.3	2,4,6- or 2,4,7-trimethylquinoline
22	171	$C_{12}H_{13}N$	0.07	1.2	propyl- or ethyl- methylquinoline/ isoquinoline
23	171	$C_{12}H_{13}N$	0.52	9.0	propyl- or ethyl- methylquinoline/ isoquinoline
24	187	$C_{13}H_{17}N$	0.39	6.7	me^4- or ethyl-me^2- or et^2- or butyl- or propyl-methyl dihydroquinoline/ isoquinoline
25	185	$C_{13}H_{15}N$	0.47	8.1	et^2- or propyl-methyl, or butyl- or me^2-ethylquinoline/isoquinoline
26	171	$C_{12}H_{13}N$	0.66	11.4	ethyl- methyl, or propylquinoline/ isoquinoline
27	187	$C_{13}H_{17}N$	0.03	0.52	me^4-, ethyl-me^2- or et^2- or butyl or propyl- methyl dihydroquinoline/ isoquinoline
28	169	$C_{12}H_{11}N$	0.54	9.4	methyl aza-acenaphthene or cyclopenta-quinoline/isoquinoline, or methyl-phenylpyridine

Table II (continued)

Peak #	Molecular Weight	Formula	Concentration Parts-per-thousand in the basic fraction	Concentration Parts-per-million in SRC oil	Compound Name
29	183	$C_{13}H_{13}N$	0.47	8.1	ethyl- or me^2- aza-acenaphthele (I) or methylcyclopentaquinoline/isoquinoline (II)
30	187	$C_{13}H_{17}N$	0.81	14.1	me^4- or ethyl-me^2- or et^2- butyl-, or propyl-methyl dihydroquinoline/ isoquinoline
31	169	$C_{12}H_{11}N$	1.66	28.8	methyl- aza-acenaphthene or cyclopenta-quinoline or methyl-phenylpyridine
32	169	$C_{12}H_{11}N$	1.33	23.1	methyl- aza-acenaphthene or cyclopenta-quinoline/isoquinoline, or methyl-phenylpyridine
33	183	$C_{13}H_{13}N$	1.41	24.5	ethyl- or me^2- aza-acenaphthene or ethyl- or me^2- cyclopentaquinoline/isoquinoline or ethyl- or me^2- phenylpyridine
34	169	$C_{12}H_{11}N$	1.22	21.2	methyl aza-acenaphthene or cyclopenta-quinoline/isoquinoline, or methyl-phenylpyridine
35	169	$C_{12}H_{11}N$	0.36	6.2	methyl aza-acenaphthene or cyclopenta-quinoline/isoquinoline, or methyl-phenylpyridine
36	169	$C_{12}H_{11}N$	0.26	4.5	same as peak number 35
37	183	$C_{13}H_{13}N$	0.99	17.2	ethyl- or me^2- aza-acenaphthene, or methyl-cyclopentaquinoline/isoquinoline or ethyl- or me^2-phenylpyridine
38	183	$C_{13}H_{13}N$	0.71	12.3	same as peak number 37
39	183	$C_{13}H_{13}N$	0.75	13.0	same as peak number 37
40	183	$C_{13}H_{13}N$	3.25	56.5	same as peak number 37

Table II (continued)

Peak #	Molecular Weight	Formula	Concentration Parts-per-thousand in the basic fraction	Concentration Parts-per million in SRC oil	Compound Name
41	183	$C_{13}H_{13}N$	0.72	12.5	same as peak number 37
42	183	$C_{13}H_{13}N$	0.37	6.4	same as peak number 37
43	183	$C_{13}H_{13}N$	0.91	15.8	same as peak number 37
44	197	$C_{14}H_{15}N$	1.16	20.1	me^3- or methyl-ethyl-propyl aza-acenaphthene, or cyclopentaquinoline/isoquinoline, or phenylpyridine
45	179	$C_{13}H_9N$	0.35	6.1	a acridine
46	179	$C_{13}H_9N$	1.56	27.1	benzoquinoline/benzoisoquinoline
47	179	$C_{13}H_9N$	1.96	34.1	benzoquinoline/benzoisoquinoline
48	193	$C_{14}H_{11}N$	2.10	36.5	methylacridine, or methylbenzoquinoline/isoquinoline

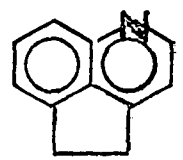
key

me^2 = dimethyl- et^2 = diethyl- me^3 = trimethyl-

me^4 = tetramethyl = reference, figure 2 a = identification confirmed by GC/MS

b = identification by reference mass spectra

quinoline/isoquinoline = quinoline or isoquinoline

I =  (aza-acenaphthene)

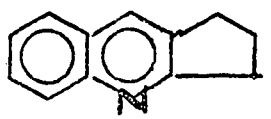
II =  (cyclopentaquinoline-2,3-dihydro)

TABLE III

Mass-spectral Data on Alkyl Quinolines

Compound	% intensities of most important ions					
	M^+(171)	M-1	M-15	M-28	M-29	M-42
3-methyl,4-ethylquinoline	80	38	100	41		23
3-methyl-1,2-ethylquinoline	77	100	4	43		1
2-isopropylquinoline	51	33	100	47		24
8-n-propylquinoline	49	28	100	50		46
5-n-propylquinoline	66	7	15	43	100	7
4-n-propylquinoline	82	77	29	100		4
2-n-propylquinoline	30	16	31	100		7
2,4,7-trimethylquinoline	100	36	22	3		8
3,4,7-trimethylquinoline	100	60	72	4		8
2,4,8-trimethylquinoline	100	38	20	1		4
2,4,6-trimethylquinoline	100	53	22	1		5
2,3,4-trimethylquinoline	100	72	46	8		16
2,6,8-trimethylquinoline	100	75	76	9		8
	M^+(185)	M-1	M-14	M-15	M-28	M-42
2,4-diethylquinoline	59	90	100	30	14	3
3,4,5,8-tetramethylquinoline	100	68		60	2	2
3,4,6,7-tetramethylquinoline	100	43		72	2	2
2,4,6,8-tetramethylquinoline	100	48		40	1	2
2,4,6,7-tetramethylquinoline	100	41		33	1	2

Technical Reports to DOE (ERDA)

1. Progress Report for the Period February 1, 1976 - January 31, 1977, Report Number COO-2856-1.

2. Progress Report for the Period February 1, 1977 - January 31, 1978, Report Number COO-2856-2.

3. Progress Report for the Period November, 1977 - April, 1978, Report Number COO-2856-3.

4. Progress Report for the Period September, 1978 - November 1978, Report Number COO-2856-4.

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R. V. Schultz, J. W. Jorgenson, M P. Maskarinec, M. Novotny and L. J. Todd, "Characterization of Polynuclear Aromatic and Aliphatic Hydrocarbon Fractions of Solvent-Refined Coal by Glass Capillary Gas Chromatography/Mass Spectrometry," Fuel, 58, 783-789 (1979).

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