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Identification of Organic Chlorines and Iodines in the Extracts from Hydrotreated Argonne Premium Coal Residues

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Received February 17, 2007

Chlorine and bromine in coals have not only technological and environmental impacts on coal utilization^{1–3} but also a significance in geochemistry.^{4,5} Many attempts have been made for investigating their contents, modes of occurrence, and origin in coals.^{6–12} Unfortunately, to our knowledge, there are few reports concerning the existing forms of organic halogens (OHs) on a molecular level up to now. In a previous paper,¹³ our group first reported the molecular structures of six organic chlorines (OCs) and two organic bromines (OBs) identified from four Chinese bituminous coals with gas chromatography mass spectrometry (GC/MS). Successful identification of the OCs and OBs mainly resulted from detailed fractionation by sequential extraction. These results prompt us to find OHs, especially organic fluorines and iodines, from other coals. In another investigation,¹⁴ our group found that Pd/C catalyzed the release of organic nitrogens, especially aniline and alkylanilines from two Chinese coal residues during hydrotreatments (HTs). The results from a further investigation by our group show that a series of organic sulfurs (OSs) were released from the Upper Freeport (UF) coal residue during noncatalytic HT and that the released OSs were removed by Ni-catalyzed HT.¹⁵ These results suggest that some heteroatom-containing organic species can be released from a macromolecular network of coals by HTs.

Coals themselves usually contain more or less solvent-soluble portion (SSP). Many organic compounds have been detected from the SSP.^{16,17} To avoid the disturbance of SSP on the analysis of

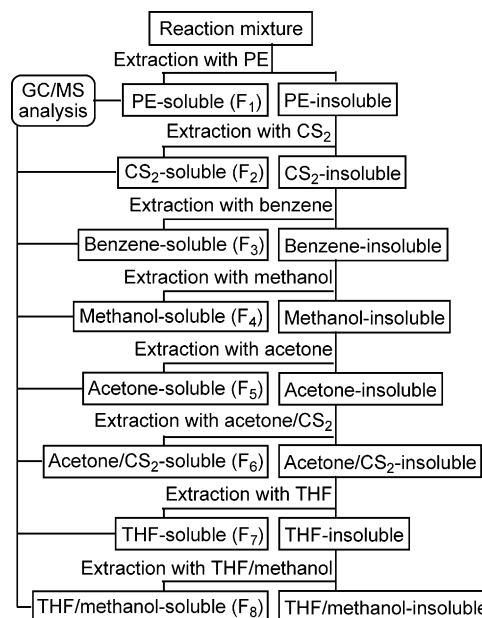


Figure 1. Extraction procedure used on the mixtures from the hydrotreated residues.

Table 1. Proximate and Ultimate Analyses of Coal Samples

coal	proximate analysis (wt %)			ultimate analysis (wt %, daf)						
	M_{ad}	A_d	V_{daf}	C	H	N	S_o^a	O^b	Cl	
P8	1.65	9.25	41.67	84.95	5.43	1.68	0.91	6.90	0.12	
UF	1.13	13.18	31.62	88.08	4.84	1.60	0.76	4.72	0.00	
P3	0.65	4.77	19.53	91.81	4.48	1.34	0.51	1.66	0.20	

^a Organic sulfur. ^b By difference.

OHs released from coals, in the present study, we used a solvent-insoluble fraction (i.e., residue) from three Argonne Premium coals as reactants and examined the release of OHs from the residues during noncatalytic and Ni-catalyzed HTs under relatively mild conditions.

Table 1 shows the proximate and ultimate analyses of three Argonne Premium coals, i.e., Pittsburgh No. 8 (P8), UF, and Pocahontas No. 3 (P3) coals. The residues used as reactants are tetrahydrofuran (THF)/carbon disulfide (CS₂) (vol/vol 2:1) insoluble fractions from the three coals. The extraction procedure of raw coals was reported elsewhere.¹⁷ After exhaustive extraction, THF and CS₂ remaining in the residues were removed by extraction with acetone. No compounds, except for THF, CS₂, and acetone, were detected with GC/MS in the extraction solution. The residues were dried in vacuum at 100 °C for 24 h. All of the solvents used were purchased from Aldrich Chemical Co., Inc. and were distilled before use. GC/MS analyses showed that no OHs were contained in the distilled solvents. Catalyst Ni (stabilized nickel, N-103) was supplied by Nikki Chemical Co., Ltd., Japan.

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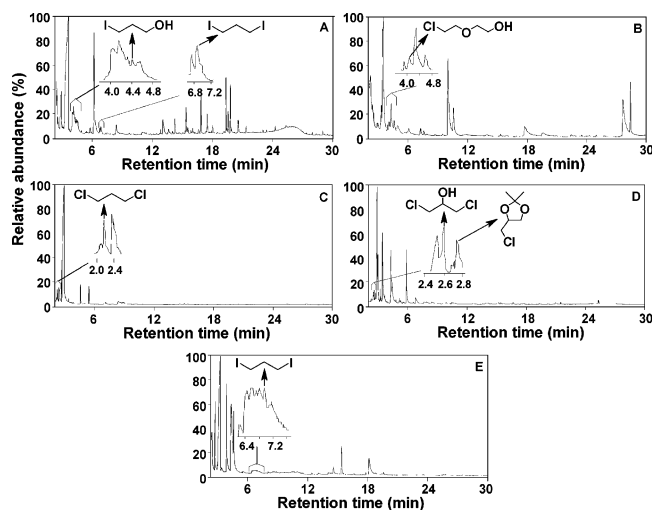


Figure 2. TICs of some extracts from HTs of the coal residues. (A) F_4 from noncatalytic HT of the UF coal residue, (B) F_4 from Ni-catalyzed HT of the P3 coal residue, (C) F_5 from noncatalytic HT of the P8 coal residue, (D) F_5 from Ni-catalyzed HT of the P8 coal residue, and (E) F_8 from noncatalytic HT of the P3 coal residue.

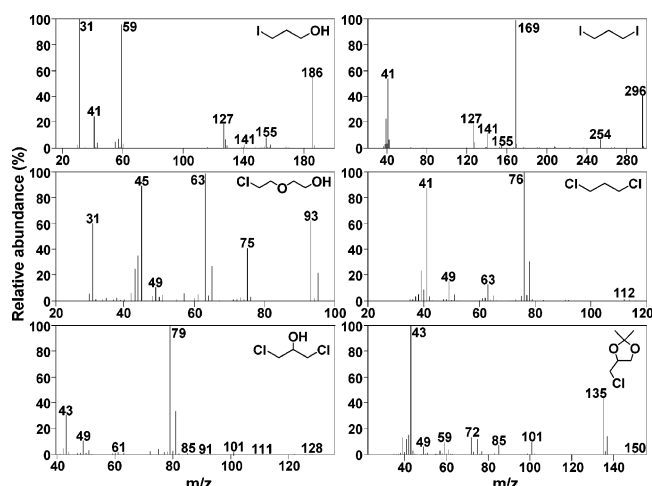


Figure 3. Mass spectra of OCs and OIs detected in some extracts from the hydrotreated coal residues.

About 1 g of a residue, 20 mL of cyclohexane, and 0 or 0.1 g of Ni were put into a 60 mL stainless-steel, magnetically stirred autoclave. After the autoclave was pressured with hydrogen to 5 MPa at room temperature, it was heated to 300 °C within 10 min and kept at that temperature for 8 h. Then, the autoclave was immediately cooled to room temperature in an ice-water bath. The reaction mixture was taken from the autoclave with petroleum ether (PE, bp = 30–60 °C) and fractionated into fractions 1–8 (denoted as F_1 – F_8) by sequential extraction with PE, CS_2 , benzene, methanol, acetone, acetone/ CS_2 (vol/vol, 2:1), THF, and THF/methanol (vol/vol, 1:2) under a nitrogen atmosphere in a Soxhlet extractor, as shown in Figure 1. The fractions were analyzed using a GC/MS system (Hewlett-Packard 6890/5973) equipped with a capillary column coated with HP-5MS (cross-link 5% PH ME siloxane, 30 m \times 0.25 mm i.d., 0.25 μ m film thickness) and a quadrupole analyzer and operated in electron-impact (70 eV) mode. The mass range scanned was from 30 to 500 amu. Data were acquired and processed using Chemstation software. The OHs were identified by comparing mass spectra with NIST98 library data.

Figure 2 exhibits the total ion chromatograms (TICs) of some fractions. Corresponding mass spectra are displayed in Figure 3. All of the mass spectra are consistent with corresponding authentic ones from the NIST98 library data in high match qualities (>90%), as seen in the Supporting Information.

As Figure 2A shows, two organic iodines (OIs), i.e., 3-iodopropan-1-ol and 1,3-diiodopropane (DIP), were observed in F_4 from noncatalytic HT of the UF coal residue. DIP was also detected in F_8 from noncatalytic HT of the P3 coal residue, as shown in Figure 2E. Although we carefully checked TIC of F_4 from noncatalytic HT of the P3 coal residue, we failed to find DIP in the fraction. DIP should originally be present in the reaction mixtures from noncatalytic HT of UF and P3 coal residues, because subsequent fractionation, i.e., sequential extraction, is much milder than the HT. However, at present, we cannot clearly understand the reason why DIP was detected in different fractions from noncatalytic HT of different coal residues. The difference in the strength of noncovalent bonds (NCBs) connecting DIP with other organic species between the two reaction mixtures could be responsible for DIP release from different fractions; i.e., the NCBs in the reaction mixture from noncatalytic HT of the P3 coal residue could be much stronger than those from noncatalytic HT of the UF coal residue. Thus far, to our knowledge, no reports have been issued on the identification of any OI from any coal.

As OCs, 2-(2-chloroethoxy)ethanol and 1,3-dichloropropane were detected in F_4 from Ni-catalyzed HT of the P3 coal residue (Figure 2B) and in F_5 from noncatalytic HT of the P8 coal residue (Figure 2C), respectively. Two OCs, i.e., 1,3-dichloropropan-2-ol and 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane, were detected in F_5 from Ni-catalyzed HT of the P8 coal residue (Figure 2D). It is interesting that all of the OCs detected in the reaction mixtures from Ni-catalyzed HT of both coal residues contain oxygen. Ni shows an excellent activity and selectivity for the hydrogenation of aromatic rings; e.g., di(1-naphthyl)-methane was predominantly hydrogenated over Ni under mild conditions.¹⁸ The release of the oxygen-containing OCs from Ni-catalyzed HT of both coal residues could be related to the excellent activity and selectivity of Ni for aromatic-ring hydrogenation, by which some covalent bonds and NCBs connecting precursors of the oxygen-containing OCs and macromolecular aromatic moiety may be destroyed. No OCs were detected in any extracts from either noncatalytic or Ni-catalyzed HT of the UF coal residue, which is consistent with data from the ultimate analysis shown in Table 1, in which UF coal contains no OCs.

All of the above OHs were not identified either in the extracts from four Chinese bituminous coals reported¹³ or in the extracts of the three Argonne Premium raw coals. They may structurally be integrated in the macromolecular organic matrix of coal,^{9,19} so that releasing them is quite difficult in the process of Soxhlet extraction. Because conventional coal conversion processes are usually performed under much severer conditions, disadvantageous effects of the OHs and their products on the coal conversion processes should be considered, although their precursors are present in the coals in very low concentrations.

In summary, our results show that some OCs and OIs are released from three Argonne Premium coal residues during noncatalytic and Ni-catalyzed hydrotreatments at 300 °C. The OHs may be a moiety of organic macromolecular species in the Argonne Premium coals.

Acknowledgment. This work was subsidized by the Special Fund for Major State Basic Research Project (projects G1999022101 and 2004CB217601), the Research Funds for the Doctoral Program of Higher Education (project 20020290007), National Natural Science Foundation of China (projects 20076051, 90410018, and 20676142), the Key Project of Chinese Ministry of Education (project 104031), the Graduate Student Creative Program of Jiangsu Province (project xm04-45), and the Program of the Universities in Jiangsu Province for the Development of High-Tech Industries (project JHB05-33). Ni was offered by Nikki Chemical Co., Ltd. of Japan. The authors are grateful to them.

Supporting Information Available: Comparison of mass spectra of the detected OCs and OIs with authentic ones from the NIST98 library database. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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