

decomposition, while FSHN and MMNG profiles are dominated by siderite decomposition.

10. CO<sub>2</sub>, CO, H<sub>2</sub>, and H<sub>2</sub>O show possible correlations through char-gasification and water gas shift reactions.

11. H<sub>2</sub>O generation is generally dominated by hydrated mineral decomposition.

12. H<sub>2</sub>S evolution appears to be governed by FeS<sub>2</sub> decomposition and organosulfur compound decomposition as modified by H<sub>2</sub>S capture by iron carbonates.

13. H<sub>2</sub>S evolution quantitation roughly follows FeS<sub>2</sub> content. KIMR, NAKY, WDFD, and WNZN have high FeS<sub>2</sub> contents and evolve around 10 cm<sup>3</sup>/g shale of H<sub>2</sub>S. PHOS, LLNA, FSHN, AP24, TSTB, MMNG, GOVT, and BROT have low concentrations of pyrite and evolve less than 4 cm<sup>3</sup>/g shale.

14. Methylthiophene amounts follow the organic sulfur content. Marine shales have high org S/org C ratios and exhibit relatively large amounts of methylthiophene. Lacustrine shales have low ratios and evolve a relatively small amount of methylthiophene.

15. The acetic acid  $T_{\max}$  value is on the leading edge of

hydrocarbon generation (400-440 °C) except for AP24, which has its largest maximum at 256 °C.

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## Appendix

Tables VIII and IX are included to provide a complete listing of the  $T_{\max}$  values for individual hydrocarbon evolution, and total evolution (when determined) for clarity. Table VIII values are also shown in Figure 1.

**Registry No.** H<sub>2</sub>, 1333-74-0; CH<sub>4</sub>, 74-82-8; C<sub>2</sub>H<sub>4</sub>, 74-85-1; C<sub>2</sub>H<sub>6</sub>, 74-84-0; C<sub>3</sub>H<sub>8</sub>, 74-98-6; C<sub>4</sub>H<sub>10</sub>, 106-97-8; H<sub>2</sub>O, 7732-18-5; CO, 630-08-0; CO<sub>2</sub>, 124-38-9; CH<sub>3</sub>CO<sub>2</sub>H, 64-19-7; H<sub>2</sub>S, 7783-06-4; thiophene, 110-02-1; methylthiophene, 25154-40-9.

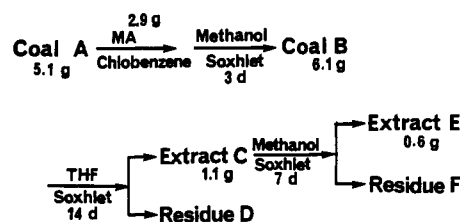
# Communications

## Strong Adsorption of Unreacted Maleic Anhydride in Coal during Diels-Alder Reaction

*Sir:* The Diels-Alder reaction using maleic anhydride (MA) has been used to study coal structure and reactivity.<sup>1-3</sup> In these studies, unreacted MA was removed from the produced adducts by washing or extraction with hot water for 5-24 h, because MA easily dissolves in water. Average weight gains of 15-30 wt % were obtained after the reaction, followed by the removal of unreacted MA. The occurrences of ester formation of MA with coal and polymerization of MA were ruled out experimentally,<sup>1,2</sup> so incorporated MA was regarded as Diels-Alder adducts. Very recently, Nishioka et al.<sup>4</sup> and Zherakova et al.<sup>5</sup> applied this procedure to coals of various rank.

It was reported in our recent paper<sup>6</sup> that charge-transfer complexes were induced by solvent soaking or exist in raw coal. Solvent-induced charge-transfer complexes are relatively strong, because the complexes are not completely disrupted by pyridine during Soxhlet extraction. This suggests that coal strongly interacts with small molecules that are electron donors and acceptors and that these compounds in such interacted complexes are recovered with difficulty by simple procedures such as solvent washing and extraction.

Since MA is known to be a good electron acceptor,<sup>7</sup> MA may also be strongly adsorbed in coal due to charge-transfer complexation during a Diels-Alder reaction step. Therefore, in this Communication, strongly adsorbed MA is investigated. Quantification of physically adsorbed MA



**Figure 1.** Recovery procedure of unreacted maleic anhydride in Pittsburgh No. 8 coal.

is a very difficult task. Here, partial recovery of unreacted MA is attempted from products formerly regarded as adducts, and positive evidence for significant quantities of strongly adsorbed MA in coal is reported. Careful differentiation must be made between chemically reacted adducts and physically adsorbed maleic anhydride.

Coal samples were obtained from the Premium Sample Program at Argonne National Laboratory. Their elemental analyses are given in Table I.<sup>8</sup> Coal particles of -100 mesh size were used except Wyoming coal which was -20 mesh size.

Pittsburgh No. 8 coal (5 g) and MA (3 g) were mixed in 100 mL of chlorobenzene in a 250-mL flask under dry N<sub>2</sub> and magnetically stirred at 115 ± 3 °C for 7 days. Chlorobenzene was removed from the cooled mixture on a rotary evaporator, prior to mixing with methanol, filtering, and rinsing with methanol several more times.

Recovery of physically incorporated MA from the Pittsburgh No. 8-MA adduct was attempted following the scheme in Figure 1. The adduct was Soxhlet-extracted with methanol for 3 days, and then with tetrahydrofuran (THF) for 2 weeks. The THF extract was further Soxhlet-extracted with methanol for 1 week. Then, coal A to residue F (see Figure 1) were obtained. These samples

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 (6) Nishioka, M.; Gebhard, L. A.; Silbernagel, B. G. *Fuel*, in press.  
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Table I. Elemental Analyses of Argonne Premium Samples (wt %)

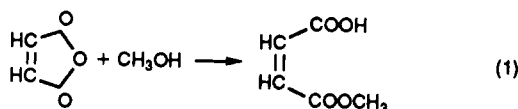
symbol	coal	H <sub>2</sub> O	ash	element (% daf)			
				C	H	N	S
ND	Beulah Zap seam from North Dakota	32.24	6.59	72.94	4.83	1.15	0.89
WY	Wyodak-Anderson seam from Wyoming	28.09	6.31	75.01	5.35	1.12	0.69
IL	Herrin (Illinois No. 6) seam from Illinois	7.97	14.25	77.67	5.00	1.37	5.71
PITT	Pittsburgh (No. 8) seam from Pennsylvania	1.65	9.10	83.20	5.32	1.64	2.41
UF	Upper Freeport seam from Pennsylvania	1.13	13.03	85.50	4.70	1.55	0.51
POC	Pocahontas (No. 3) seam from Virginia	0.65	4.74	91.05	4.44	1.33	0.51

were analyzed by FTIR spectroscopy with an IBM 97/IR using photoacoustic detection,<sup>9</sup> and extract E was further analyzed by gas chromatography (GC).<sup>10</sup>

Coal samples (2.5 g) were extracted with 200 mL of pyridine for 72 h in a Soxhlet apparatus under a nitrogen atmosphere, while Upper Freeport coal was extracted for 30 days. The coal residues were Soxhlet-rinsed with methanol for 24 h, and then both coal extracts and residues were dried in a vacuum oven at 95 °C overnight. Procedures of the O-methylation and the 2 N HCl washing were previously described.<sup>6</sup>

The weight gain by the Diels-Alder reaction for Pittsburgh No. 8 coal was 20 wt % (coal B in Figure 1). This value is consistent with reported results.<sup>2</sup> Extraction using methanol was more effective than water to remove solvent (chlorobenzene) and MA as reported in our paper.<sup>4</sup> Incorporated MA after extraction with hot water has been regarded as chemically reacted MA.<sup>1-3,5</sup> If all unreacted MA can be removed with hot water or methanol, the THF extract from coal B should not contain a significant amount of MA, because coal B was fully extracted with methanol.

Extract E, which was 60 wt % yield in the total weight gain, was recovered as methanol soluble from extract C. It is known that MA promptly reacts with methanol at room temperature and produces monomethyl ester (eq 1).<sup>11</sup>



This ester in extract E was analyzed by using GC, and approximately 12 wt % MA as the monomethyl ester was quantitated in extract E. This result shows that a large amount of unreacted MA is physically retained in coal after the conventionally used Diels-Alder reaction step, although it was difficult to quantitate retained MA.

The IR spectra of coal A to residue F are shown in Figure 2. Two absorption bands at about 1780 and 1850 cm<sup>-1</sup>, assigned to the mechanical coupling of the anhydride carbonyl vibrations, were not observed in coal B to residue F. This supports the esterification of the anhydride group with methanol. Detection of the double bond (1590–1596 cm<sup>-1</sup>) of physically retained MA or its ester was impossible because of strong absorption of this region from coal. The large difference of carbonyl content between coal B and residue D or between extract E and residue F can be interpreted as the amount of physically incorporated MA between these two samples, because the carbonyl content between these samples should be nearly equal if the incorporated MA originates from the chemical reaction.

Several questionable issues concerning the Diels-Alder reaction in coal can be explained by unreacted MA strongly

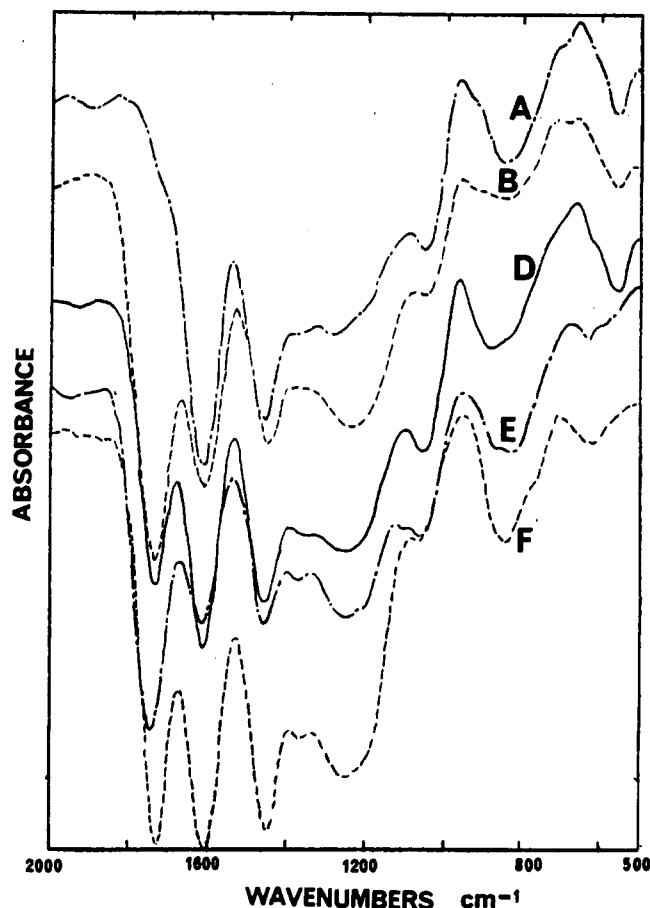


Figure 2. Infrared spectra of coal A to residue F (see Figure 1).

adsorbed in coal. As discussed by Larsen et al.,<sup>12</sup> it is improbable that weight increases of 15–30 wt % can be attributed to the products of MA and the anthracene structural unit in coal, because 1/3 of the carbons in coal would have to be in reactive polycyclic aromatic compounds. Polycyclic aromatic hydrocarbons containing the anthracene structural unit in coal extracts and coal-derived liquids are less abundant than angular types of compounds such as phenanthrene, chrysene, and picene, and cata-condensed polycyclic aromatic hydrocarbons are less important upon increasing in aromatic ring numbers.<sup>13</sup> A significant amount of MA seems to be adsorbed.

The weight gains of MA after the reaction were 15 to 30 wt % regardless coal rank.<sup>4,5</sup> Enhancement of pyridine extraction yields was found for medium- and low-volatile bituminous coals.<sup>3</sup> The reason for this was interpreted to be that, with condensed aromatics, the addition of the maleic anhydride to the edge of the molecule will disrupt the stacking interaction between polycyclic aromatic com-

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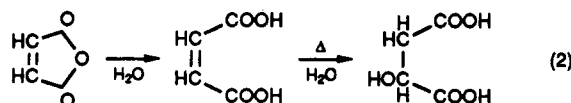
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**Table II. Pyridine Incorporations (wt %) from the Mass Balance after Pyridine Extractions Followed Drying at 95 °C under Vacuum**

coal	recovery after drying at 95 °C under vacuum of original coals	recovery after pyridine extraction of								
		original coals			2N HCl-washed coals			O-methylated coals		
		ext	res	total %	ext	res	total %	ext	res	total %
ND	67	10	63	109	12	60	107	16	54	104
WY	72	18	62	111	15	62	107	24	51	104
IL	92	37	65	111						
PITT	99	39	62	102						
UF	99	41	63	105						
POC	99	5	94	100						

pounds.<sup>3</sup> On the other hand, reduction of pyridine extraction yields was found for high-volatile bituminous coals, although a nearly equal amount of MA was incorporated into high-volatile bituminous coals as well.<sup>4</sup> This result was rationalized by solvent-induced association during soaking in the Diels–Alder reaction step.<sup>4</sup> It is suggested from the results shown above that most MA is physically adsorbed in high-volatile bituminous coals and this adsorbed MA cannot contribute to breaking the stacking interactions.

The increase in pyridine extractability was found for low-rank coals.<sup>4</sup> This may be explained as follows. When water is used during the removal step of MA, MA is hydrolyzed to maleic acid at room temperature or malic acid at high temperature (eq 2).<sup>11</sup> Therefore, rinsing the



mixture of adsorbed MA and lower rank coals with water is effective in reducing ionic forces and enhance their pyridine extractability, because maleic or malic acid is formed and neutralize cations abundant in lower rank coals.<sup>6</sup> Similar acid washing effect on solvent extractability by using an organic acid was reported by Gouker and Liotta<sup>14</sup> who used citric acid.

Larsen and Lee<sup>2</sup> investigated the effect of solvent swelling on the diffusion rate of MA in two high-volatile bituminous coals (Illinois No. 6 and Bruceton coals). They regarded increased weights as products of the Diels–Alder reaction. Then, they concluded that the rate of this reaction was diffusion controlled but was independent of the degree of swelling of the coals. These findings may have been obtained from the result of a significant amount of physically adsorbed MA and not from the results of the chemically reacted MA.

Only for medium- and low-volatile bituminous coals, both the stack thickness,  $L_c$ , and the length,  $L_a$  decreased after the reaction.<sup>5</sup> A change in the [002] diffraction band was also observed for low-volatile bituminous coal.<sup>10</sup> The adducts of coals containing more than 90% C are much more extractable than the starting coal is.<sup>3,4</sup> Therefore, some degree of the Diels–Alder reaction occurs in higher rank coals; however, caution should be exercised when drawing conclusion based on the Diels–Alder reaction in lower rank coals.

The reason for a large amount of physically retained MA is unknown. I propose charge-transfer complexation be-

tween MA and coal, because MA is a good electron acceptor. We recently reported evidence of charge-transfer complexes in coal, although the observation of a charge-transfer band was difficult.<sup>6</sup> In fact, on the basis of ESR observations Zherakova and Kochkanan<sup>5</sup> suggested that MA is arrested at the charge-transfer complex stage during the Diels–Alder reaction. However, they did not consider the presence of physically retained MA in the products.

If MA is strongly adsorbed in coal as an electron acceptor by forming charge-transfer complexes, an electron donor solvent would likewise be expected to be strongly adsorbed in coal. We have found that pyridine is physically retained in both extracts and residues in the range of 1–10 wt % after drying under high vacuum.<sup>15–19</sup> Pyridine is an electron donor. Since retention of pyridine in various rank coals has not been systematically studied, retained pyridine was examined for the Argonne Premium Samples as listed in Table II.

The weight loss of original coals, after drying overnight at 95 °C under vacuum, coincided with water content within  $\pm 1$  wt %. Extraction residues were Soxhlet-rinsed with methanol for 1 day after pyridine extraction, and both extracts and residues were dried under the same condition described above. Their total weights were compared with those of the dried starting coals, and excess weight was attributed to retained pyridine.

The pyridine incorporation was measured for original coals and two 2 N HCl-washed or O-methylated low-rank coals as shown in Table II. To decrease pyridine retained by forming pyridinium ion or by forming hydrogen bonds with coals, two low-rank coals were washed with 2 N HCl to neutralize anions or O-methylated to cap off –COOH and –OH groups. The amount of the incorporation is rank-dependent. The weight percent of pyridine retention in lower rank coals is significant even after HCl-washing or O-methylation. It is very difficult to remove pyridine even with a lower boiling point than MA except low-volatile bituminous coal, although retained pyridine is easily exchangeable with free pyridine.<sup>15</sup> This implies that pyridine is strongly adsorbed in coal by charge-transfer complexes similarly to MA.

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**Registry No.** MA, 108-31-6.

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