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Coal Solubilization with Cadmium and Butyl Iodide under Mild Conditions

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Several coals were treated with Cd and butyl iodide at 130 °C under atmospheric pressure to obtain more detailed information concerning coal-solubilization for a metal–alkyl halide system under mild conditions. The treatment effectively converted coal to benzene-soluble products with an optimum yield of 57wt%, somewhat less than that obtained in a Zn–butyl iodide system. There was no correlation between the rank of coal used and the benzene solubility. Reactions of model compounds were also carried out under similar conditions. Polynuclear aromatic compounds gave polybutyl-substituted and/or -addition derivatives. Although the alkyl ether linkages were easily cleaved, the aryl ether linkages were not. In addition, many butyl groups were introduced into both the aromatic and aliphatic moieties. These results suggest that the high benzene solubility is attained by an introduction of the many butyl groups, as well as cleavage of the alkyl ether linkages. Also, the introduction of butyl groups into the aliphatic moiety suggests smaller benzene solubilities of Cd-treated coal compared to those of Zn-treated coal. Because most of the products of the model compounds were similar to those obtained in the Zn–butyl iodide system, and some of the butyl groups introduced were rearranged to *s*-butyl, it is suggested that both alkyl cation reactions and alkyl radical reactions occur competitively in the Cd–butyl iodide system, as well as in the Zn–butyl iodide system.

Coal treated with Zn and butyl iodide shows remarkable benzene solubility.[1,2] Because of the mild conditions (at 130 °C under atmospheric pressure) the molecular weights of the solvent-soluble products were fairly high.[2] We showed that a high benzene extractability using the Zn–butyl iodide system could be attained by introducing many butyl groups into the aromatic moieties and by cleaving some of the aliphatic and ether linkages.[5]

We were interested in this study in order to elucidate the reasons for the high solubility and high yields of butylated products. In the present study, several types of coal were treated with butyl iodide and Cd, which belong to the same group of the periodic table as Zn. In addition, some model compounds related to coal structure were treated in the Cd–butyl iodide system in order to investigate the mechanism of solubilization in benzene.

Experimental

Coal. Elemental analyses of the coal used are listed in Table 1. A typical reaction was carried out as follows: One gram of coal, the desired weight of cadmium (100 or 40—60 mesh), and 10 ml of butyl iodide were placed in a tear-drop type flask. Being agitated, the mixture was heated at 130 °C for 0.5—5 h. After evaporation of unreacted butyl iodide, dil HCl was added in order to remove any unreacted cadmium; when 40—60 mesh cadmium was used, the mixture was washed further with dil HNO_3. The butylation product was extracted with benzene at 60 °C; after the evaporation of benzene the extract was dried under vacuum until it showed a constant weight. The solubility efficiency (E_S) is calculated by

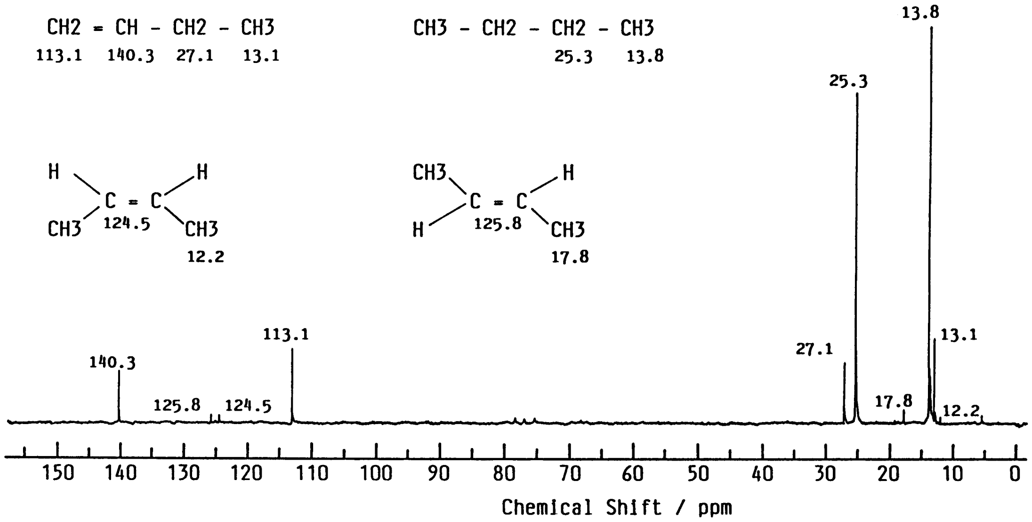


Fig. 1. ^{13}C NMR spectrum of the gases evolved from the reaction with Cd and butyl iodide.

Table 1. Ultimate Analyses of Coal (wt%)

Coal	C	H	N	O[a]	H/C	Ash
Illinois No.6	74.5	5.4	1.6	18.5	0.86	11.0
Taiheiyo	75.1	6.3	1.3	17.3	1.00	15.2
Wandoan	75.6	5.9	1.1	17.4	0.93	8.9
Akabira	80.8	5.8	2.1	11.3	0.85	7.3
Yubari	85.0	5.6	1.8	7.6	0.78	6.1
Kairan	87.0	4.9	1.3	6.8	0.67	11.5

a) By difference.

$$E_S=\frac{\text{Bu-P Yield (wt\%)}\times\text{BS (wt\%)}/100}{\text{Bu-P Yield (wt\%)}-100}.$$

This value suggests the degree of effectiveness of added butyl groups on solubilization.[2] The gas which evolved violently during butylation was trapped at −80 °C, or in a sample bag. Butane, 1-butene, and a trace amount of 2-butene isomers were identified by means of gas chromatography (GC) and the ^{1}H and ^{13}C NMR spectra at −30 °C (Fig. 1). The gas chromatograms were recorded with a Hitachi 163 spectrometer, and the ^{1}H and ^{13}C NMR spectra were taken on a JEOL JNM-FX90Q spectrometer.

Model Compound. The purchased reagents were used without purification, except for anthracene, which was used after recrystallization. Butylation was carried out under similar conditions as in the reaction of coal: One gram of a compound, 6.9 g of 100 mesh Cd, and 15 ml of butyl iodide were placed in a tear-drop type flask; the mixture was then refluxed for 1—2 h. After adding water and then dil HCl, the mixture was extracted with ether. The solvent was then removed, and the products analyzed by GC and GC-MS (glass capillary column, 25×0.25 mm, SE-52).[6,7]

Results and Discussion

Coal. At first, we treated Yubari coal with various weights of cadmium in order to confirm the effectiveness of the treatment with Cd and butyl iodide on the butylation and solubilization of coal. The reaction conditions, yields of butylated products (Bu-P), and benzene solubilities (BS) are presented in Table 2. All runs showed large yields of Bu-P and BS. The introduction of a high proportion of butyl groups seemed to be effective on BS. The effects of the reaction time showed no significance on both the Bu-P and BS; the results thus obtained from Table 2 indicate that the butylation of coal proceeds rapidly. It is clear that this treatment is effective for the butylation and solubilization of coal.

Table 2. Yields of Butylated Products (Bu-P) of Yubari Coal and Benzene Solubility (BS)

Run No.	Grain size of Cd	Cd/Coal ratio		Reaction time	Yield[a] of Bu-P	BS[b]
	mesh	g/g	mmol g^{-1}	h	wt%, daf	wt%, daf
1	40—60	3.4	30	5.0	176	36.7
2	40—60	5.2	46	3.5	183	51.1
3	40—60	6.9	61	3.3	174	56.5
4	40—60	10.3	92	1.4	194	32.4
5	100	3.4	30	0.6	187	38.9
6	100	5.2	46	0.6	177	45.4
7	100	6.9	61	0.5	169	48.8
8	100	8.6	77	0.4	159	46.0
9	100	10.3	92	0.4	170	38.4

a), b) Yields are based on original coal and butylated products, respectively.

Table 3. Number of Butyl Groups Added per 100 Original Carbon Atoms and E_S of the Butylated Yubari Coal

Run No.	No. of butyl groups/100 C				E_S[d]
	A.R.[a]	C.B.[b]	M.B.[c]	Mean	
1	16.3	18.5	18.8	17.9	0.85
2	13.7	17.7	20.6	17.3	1.13
3	12.5	16.6	18.3	15.8	1.33
4	14.5	19.7	23.3	19.2	0.67
5	18.2	21.4	21.6	20.4	0.83
6	16.8	19.4	19.1	18.4	1.04
7	14.5	17.9	17.1	16.5	1.20
8	14.1	15.4	14.6	14.7	1.24
9	12.5	17.6	17.4	15.8	0.93

a) From change of H/C atomic ratio. b) From carbon balance. c) From material balance. d) E_S=(Bu-P Yield×BS/100)/(Bu-P Yield−100).

E_S and the number of butyl groups added per 100 carbon atoms are given in Table 3. The high values of the number of butyl groups introduced also indicate that the treatment is effective for butylation. However, since the addition of butyl groups in the Cd–butyl iodide system was less effective on BS than that in Zn–butyl iodide system, most E_S are less than those shown for the Zn–butyl iodide system.[1] In coal solubilization by alkylation, as the coal becomes richer in alkyl groups the solubility in a solvent increases;[4,8] although we have also found this correlation in the Zn–butyl iodide system,[1] we did not find it in a treatment with Cd and butyl iodide.

In alkylation studies, a correlation between the coal rank and solubility has been reported;[3,4] the higher is the rank of coal, except for anthracite, the greater is the solubility. We have also found such a correlation in the Zn–butyl iodide system.[1] To investigate the effect of coal rank on BS, several types of coal (1 g) were treated with Cd (6.9 g) and butyl iodide (10 ml). The yields of Bu-P, BS, E_S, and the number of butyl groups added per 100 carbon atoms are summarized in Table 4. Although four types of coal showed almost the same Bu-P yields, their BS were varied from 40 wt% for Illinois to 20 wt% for Taiheiyo coal. And, although Kairan coal treated with Zn and butyl iodide has shown the highest BS, it also showed the low yields of Bu-P and BS in the Cd–butyl iodide system. Significantly, low E_S values indicate that the introduction of butyl groups is not very effective for the production of benzene-soluble products. The fact that there is no correlation between the coal rank and BS suggests that the solubilization of treated coal reflects the coal characteristics.

Model Compounds. As described above, treatment

Table 4. Effect of Coal Rank on the Butylation[a)]

Coal	Yield[b)] of Bu-P	BS[c)]	Butyl Groups Added per 100 C				E_S[g)]
	wt%, daf	wt%, daf	A.R.[d)]	C.B.[e)]	W.I.[f)]	Mean	
Illinois No. 6	142	39.8	8.1	12.8	11.9	10.9	1.35
Taiheiyo	139	26.0	7.9	11.0	10.9	9.9	0.93
Wandoan	140	20.7	8.0	10.6	11.1	9.9	0.72
Akabira	138	32.7	8.0	10.1	9.9	9.3	1.19
Yubari	169	48.8	14.5	17.9	17.1	16.5	1.20
Kairan	118	36.8	4.7	4.5	4.4	4.5	2.41

a) Reaction conditions: Coal/Cd(100 mesh)/BuI=1 g/6.9 g/10 ml at 130 °C for 20—30 min.
b), c) Yields (wt%, daf) are based on original coal and butylated products (Bu-P), respectively.
d—g) Notations are the same as those in Table 3.

Table 5. Conversion and Products of Polynuclear Aromatic Compounds[a)]

	Reactant		
	1-Methylnaphthalene	Phenanthrene	Anthracene
Conversion/%	85.3	93.6	100
Products[b)]	Yield of fraction/wt%		
BSD of reactant	58.4	51.6	9.9
BAD of reactant	33.9	30.2	79.4
BDAD of reactant			1.6

a) Reaction conditions: Reactant/Cd(100 mesh)/BuI=1 g/6.9 g/15 ml at 130 °C for 1—1.5 h.
b) BSD: mono and polybutyl-substituted derivatives; BAD: butyl-addition derivatives; BDAD: butyl-diaddition derivatives.

with Cd and butyl iodide can effectively butylate coals. Although this is comparable to a treatment with Zn and butyl iodide, the BS of coals treated with Cd is less than that treated with Zn. In order to determine what kind of reaction causes these large extents of butylation, as well as the smaller BS of coal treated with Cd, several model compounds related to coal structures were treated with Cd and butyl iodide.

The model compounds selected for this study were ether and aliphatic linkages containing compounds and polynuclear aromatic compounds, since it is known that ether and aliphatic linkages are characteristic bonds of coal structures and connect the aromatic moieties which comprise polynuclear aromatic components. Conversion was calculated from the amount of recovered reactant; the yields (wt%) of every reaction product were estimated based on the total products.

Every reaction product contained many components similar to those shown in the treatment with zinc.[5)] At first, 1-methylnaphthalene, anthracene, and phenanthrene were treated with Cd and butyl iodide; the conversion and the yields of the products are shown in Table 5. Three compounds showed high conversion, and yielded mono and poly-butyl substituted derivatives (BSD) and poly-butyl addition derivatives (BAD). An examination of the mass spectra of monobutyl substituted components suggests that the introduced butyl groups were not only butyl but also *s*-butyl (Table 6). The presence of BSD and BAD, as well as the occurrence of an rearrangement of the introduced butyl groups suggests that a Friedel-Crafts type alkylation as well as a radical-type alkylation also occurred competitively in treatments with Cd, as observed in the treatment with Zn.[5)] The products from 1-methylnaphthalene contained a small amount of pentylnaphthalene (1.5%), which may have resulted from a methyl attack of a butyl group. We thus expect that butyl groups are introduced not only into the aromatic moieties, but also into the aliphatic ones in the Cd-butyl iodide system. In general, the introduction of butyl groups into aromatic moieties is more effective for coal solubilization than is the introduction into aliphatic ones.[9)] Therefore 9,10-dihydrophenanthrene and 9,10-dihydroanthracene were treated with Cd and butyl iodide. For a comparison, treatments with Zn and butyl iodide were also carried out.

Table 6. Rearrangement of the Butyl Group of the Monobutyl-Substituted Products

Reactant	Yield of fraction/wt%	
	Butyl	*s*-Butyl
1-Methylnaphthalene	25.4	2.4
Phenanthrene	21.8	0.7
Anthracene	1.6	Nil
Diphenylmethane	6.6	Trace
Diphenyl ether	51.1	6.0

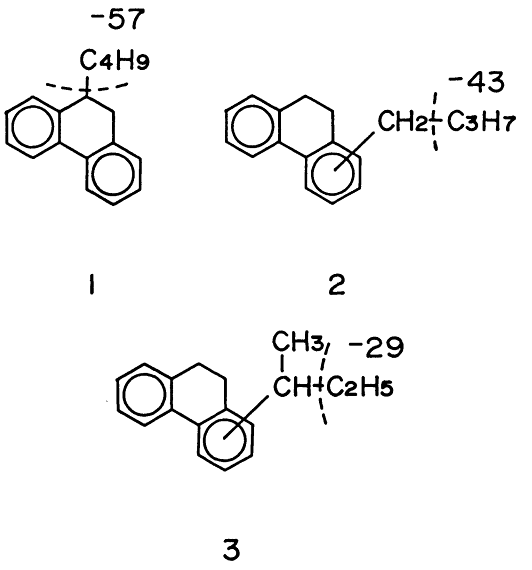
The conversions and products are summarized in Table 7. Although the treatment of 9,10-dihydrophenanthrene with Cd and butyl iodide gave a large

Table 7. Conversion and Products of 9,10-Dihydroanthracene and 9,10-Dihydrophenanthrene[a)]

	Reactant			
	Dihydrophenanthrene		Dihydroanthracene	
Metal	Cd	Zn	Cd	Zn
Conversion/%	91	90	99	90
Products[b)]	Yield of fraction/wt%			
Phenanthrene	14.6	1.7	—	—
BSD of pheanthrene	57.7	6.8	—	—
BSD of dihydrophenanthrene	21.7	39.3	—	—
Anthracene	—	—	Nil	0.4
BSD of anthracene	—	—	16.1	6.1
BSD of dihydroanthracene	—	—	66.8	54.4

a) Reaction conditions: Reactant/Cd(100 mesh)/BuI=1 g/6.9 g/15 ml at 130 °C for 1—1.5 h.
b) Notation are the same as in Table 5.

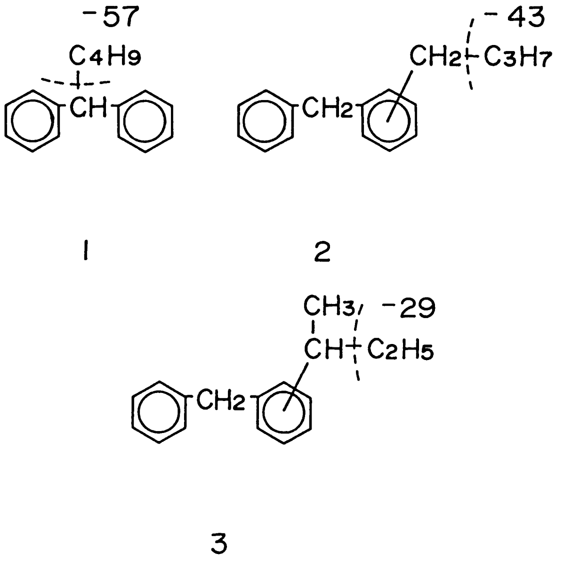
amount of phenanthrene and its BSD, treatment with Zn and butyl iodide gave only small amounts of these products. Hence, it seems that dehydrogenation easily occurred in the treatment of coal with Cd. To determine the position of the introduced butyl groups, the mass spectra of monobutyl substituted 9,10-dihydrophenanthrene were analyzed. The mass spectra of most products after a treatment with Cd showed a peak at m/z $M^+{-}57$, which is characteristic of 9-butyl-9,10-dihydrophenanthrene (**1**);[10)] the mass spectra of products treated with Zn showed peaks at $M^+{-}43$ (**2**) and $M^+{-}29$ (**3**), which indicate that butyl groups were introduced into the aromatic carbons (Scheme 1). Thus, butyl groups tend to be introduced at the 9 and 10 positions during a treatment with Cd, and at the aromatic carbons during a treatment with Zn. The results from a run on 9,10-dihydroanthracene, however, differed from those of dihydrophenanthrene. The BSD of anthracene was formed to a larger extent in the Cd treatment than in the Zn treatment, and anthracene was formed to either a small extent, or not at all. These results suggest that, in the treatment of coal with Cd and butyl iodide, some butyl groups are introduced into the aliphatic moieties in the coal structures.



Scheme 1.

Some linkages between the aromatic and hydroaromatic ring clusters in coal structures are known regarding both ether and aliphatic linkages. The model compounds containing the ether linkage selected for this study were diphenyl ether, 2-methoxynaphthalene, and dibenzyl ether. Diphenyl ether showed a 43% conversion. The products were only BSD (94.0%) of diphenyl ether; no linkage-cleavage components were observed, similar to the case of the Zn treatment. 2-Methoxynaphthalene showed a 100% conversion, and gave both BSD (18.9%) and BAD (51.4%) of 2-methoxynaphthalene, as well as both BSD (0.7%) and BAD (16.1%) of butoxynaphthalene, which was produced via a cleavage of the alkyl ether linkages followed by the introduction of butyl groups. The cleavage of the aryl alkyl ether linkage occurs to a less extent in a treatment with Cd than in those with Zn, since the products treated with Zn contained a large amount of butoxynaphthalene derivatives (33.3%).[4)] In all of the components of dibenzyl ether, the ether linkage cleaved with 100% conversion. Because of the complexity of the gas chromatogram, the percentage of components identified was meager. The products contained pentylbenzene (11.0%), and BSD (27.6%) of toluene as well as pentylbenzene. The other products were bibenzyl (2.3%), benzyltoluene (0.2%), and their BSD (5.9%). The linkage of dibenzyl ether also cleaves in a treatment with Cd, just as in the case with Zn. It is thus clear that although the aryl alkyl ether linkages are difficult to cleave, the alkyl ether linkages cleave in a reaction with Cd.

Diphenylmethane and bibenzyl were selected as model compounds containing an aliphatic linkage. Diphenylmethane showed a 78% conversion. The white solid precipitated from the reaction products with



Scheme 2.

diphenylmethane was recrystallized from chloroform, and identified to be 1,1,2,2-tetraphenylethane from an mp determination[11] as well as an examination of the spectral data of MS, ^{1}H, and ^{13}C NMR. The products contained the BSD (31.8%) of diphenylmethane, 1,1,2,2-tetraphenylethane (30.9%), as well as its BSD (16.8%). Bibenzyl showed a 54% conversion, and the products contained BSD (63.8%) of bibenzyl. Neither of the reaction products contained any aliphatic linkage-cleaved components.

As mentioned above, butyl groups are introduced not only at the aromatic positions, but also at the aliphatic positions of 9,10-dihydrophenanthrene. Accordingly, the mass spectra of monobutyl-substituted diphenylmethane isomers were also analyzed. The monobutyl-substituted diphenylmethane isomers gave characteristic fragments at *m*/*z*, M^+-57 for **1**, M^+-43 for **2**, and M^+-29 for **3** (Scheme 2).[6] Compound **1** was included in 16.7% yield; the yields of **2** and **3** are listed in Table 6. As expected, many butyl groups were introduced at the methylene carbon of diphenylmethane. These results indicate that the aliphatic linkages of coal structures are difficult to cleave by a treatment with Cd, and that many butyl groups are introduced into the aliphatic moieties of coal structures.

In view of the efficiency of the Cd treatment on coal-solubilization, it can be concluded that the benzene extractability of coal is attained by introducing many butyl groups and by the cleavage of some alkyl ether linkages. The smaller BS of Bu-P by Cd than those by Zn seems to arise from the fact that many butyl groups are introduced not only into aromatic moieties of coal structures but also into aliphatic ones; further, the aryl alkyl ether and aliphatic linkages are difficult to cleave. In addition the naphthenic structures of coal seem to aromatize due to the occurrence of a dehydrogenation of dihydrophenanthrene.

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