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Solubilization of Coal by a Treatment with Butylzinc Compounds under Mild Conditions.
—Active Species in a Zinc-Butyl Iodide System for Coal Solubilization—

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To elucidate the effectiveness of a treatment of coal with butylzinc compounds on coal solubilization, Yubari coal was treated with Bu_2Zn and/or BuZnX (X=Cl, Br, I) in the presence or absence of alkyl halide (RX). Both the treatment using Bu_2Zn or BuZnI and that with a combination of Bu_2Zn and RX (X=Cl, Br) were not very effective for coal solubilization, whereas the combination of Bu_2Zn, BuZnX (X=Cl, Br, I) and BuX (X=Cl, Br, I) was very effective. The best yield of a benzene-soluble product (BS) of Yubari coal was 96%. The ^{13}C NMR and FT-IR spectra of each BS fraction of Yubari coal treated with $^{13}CH_3I$, CH_3I, and BuI, respectively, in the presence of BuZnI and Bu_2Zn showed that the alkyl and butyl groups from RX and butylzinc compounds were introduced into the BS fractions according to addition and substitution toward aromatic moieties. The addition of alkyl groups to aromatic moieties seemed to be more effective coal solubilization than the substitution of alkyl groups. These results indicate that BuZnI, Bu_2Zn, and BuI are indispensable species in the Zn/BuI system for effective coal-solubilization.

We have found that the treatment of coal with Zn and alkyl halide (RX) accelerates coal solubilization.[1,2] The treatment of the coal with Zn and BuI under mild conditions (at 130 °C under atmospheric pressure of nitrogen) brought about a high benzene solubility of the resulting coal.[1,2] We have previously proposed that Friedel–Crafts-type and radical-type alkylations occur competitively in this reaction.[3] Treating the coal with butyl iodide and either $AlCl_3$ or ZnI_2 was found to not be as effective for solubility in benzene.[1,4] This finding excludes the predominance of the Friedel–Crafts-type reaction in the Zn/BuI system.

The reaction conditions used with a run of coal by Zn and BuI were similar to those for the preparation of both dibutylzinc (Bu_2Zn) and butylzinc iodide (BuZnI), as shown in Eq. 1.[5,6]

$$2C_4H_9I + 2Zn \longrightarrow 2C_4H_9ZnI \rightleftarrows (C_4H_9)_2Zn + ZnI_2 \quad (1)$$

Therefore, these two butylzinc compounds seem to be formed in situ in the Zn/BuI system, which was applied for the run of coal solubilization. We have estimated that butylzinc compounds (Bu_2Zn and BuZnI) play important roles as active species in the Zn/BuI system.[7]

As a result of the present study, we report on the details concerning coal solubilization using several combinations of butylzinc compounds and/or butyl halide (halogen atom: Cl, Br, and I) in order to determine a mechanism for coal solubilization.

Experimental

Yubari coal (C, 85.5 wt%; H, 6.0 wt%; O(diff), 8.5 wt%; Ash 6.0 wt%) was ground to pass 100 mesh and dried to a constant weight at 60 °C under a vacuum.

Preparation of Butylzinc Compounds. Both Bu_2Zn and BuZnX (X=Cl, Br, I) reagents were prepared according to the reported methods, and were treated under a dry nitrogen atmosphere.[5,6,8] Bu_2Zn was prepared as follows: 52.3 g (Zn 0.82 mol; Cu 0.082 mol) of Zu/Cu couple, 36.8 g (0.20 mol) of butyl iodide, and 27.4 g (0.20 mol) of butyl bromide were placed in a tear-drop-type flask, the mixture being stirred magnetically under reflux. After removing unreacted butyl iodide under reduced pressure, Bu_2Zn was distilled at 34—35 °C/133 Pa. BuZnI was prepared by two methods.[6,9] First, 35 g (Zn 0.48 mol; Cu 0.055 mol) of Zn/Cu couple, 12.5 g (0.068 mol) of butyl iodide, and 8.3 g of ethyl acetate (0.094 mol) were placed in a three-necked flask, and the mixture was heated at 90 °C while being agitated. Then, 42.3 g of butyl iodide was added dropwise into the mixture and stirred for 1 h. After filtration of the mixture, ethyl acetate and unreacted butyl iodide were removed under vacuum. Tetrahydrofuran (THF) was added to the resulting BuZnI until the concentration of BuZnI reached 2.5 $\mathrm{mol\,dm^{-3}}$. The other method was conducted as follows. First, 15 g of Bu_2Zn (0.08 mol) was added to an excess amount (0.19 mol) of ZnX_2 (X=Cl, Br, I) and stirred at 70 °C for 1 h. The supernatant solution of this reaction mixture of BuZnI and Bu_2Zn was collected (Eq. 4).

Alkylation of Coal. Yubari coal (1 g) and the desired amount of Bu_2Zn and/or BuZnX (X=Cl, Br, I), along with RX when it was needed, were placed either in a 100 ml tear-drop-type flask or a 100 ml autoclave, by replacing its atmosphere with nitrogen at room temperature under 1 atm. The mixture was stirred at a temperature ranging from 130 to 180 °C for a given period and then poured slowly into water. The butylated product (Bu-P) was washed with dilute hydrochloric acid followed by hot water until no halide ion was detected. A benzene soluble product (BS) was obtained by benzene extraction of Bu-P at 60 °C. The yields of Bu-P and BS were based on Yubari coal and Bu-P, respectively.

Instrumental Analysis. The FT-IR spectra were measured according to a diffuse reflectance procedure using a JASCO FT/IR-3 spectrometer. The samples were grounded with KBr prior to measurements. The ^{1}H and ^{13}C NMR spectra were taken on a JEOL JNM FX 90Q and on a GSX 400 spectrometer. The NMR spectra were measured in $CDCl_3$ with tetramethylsilane (TMS) used as an internal standard.

Results and Discussion

Coal Solubilization with Butylzinc Compounds. Table 1 shows the solubilization results of Yubari coal treated with either Bu_2Zn or BuZnI. The treatment of coal with either Bu_2Zn or BuZnI was not very effective for coal solubilization.

Since the addition of BuI to Bu_2Zn and/or BuZnI was very effective for coal solubilization except for the case of BuZnI in THF,[7] a detailed study of how added BuI works in the above-mentioned systems was carried out. Figure 1 (Bu_2Zn) and Fig. 2 (the mixture of BuZnI and Bu_2Zn) show the effect of the addition of BuI on the yields of Bu-P and BS. BuZnI was used in its saturated solution of Bu_2Zn (Fig. 2). With an increasing amount of BuI, the yields of Bu-P and BS increased up to 193 wt% and 93.7 wt% in the cases of Bu_2Zn and 189 wt% and 93.9 wt% in the cases of the mixture, $BuZnI/Bu_2Zn$, respectively. These solubilities are comparable to those attained in a run of coal with zinc and butyl iodide.[1] In the case of a mixture of BuZnI and Bu_2Zn, since even the addition of a small amount of BuI was effective for coal solubilization, BuZnI seems to be produced in situ and to act as one of active species in the reaction of coal with Bu_2Zn and BuI, as shown in Eqs. 2, 3, and 4.[9]

$$\text{Coal-H} + Bu_2Zn + BuI \longrightarrow \text{Coal-Bu} + BuZnI + \text{Butane} \qquad (2)$$

$$\text{Coal-2H} + Bu_2Zn + 2BuI \longrightarrow \text{Coal-2Bu} + ZnI_2 + 2\text{Butane} \qquad (3)$$

$$Bu_2Zn + ZnI_2 \longrightarrow 2BuZnI \qquad (4)$$

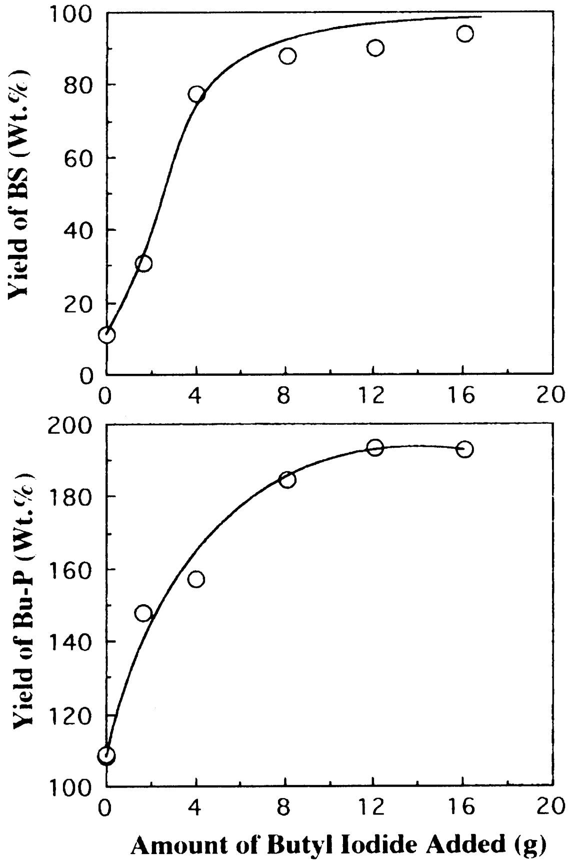

Fig. 1. Effect of addition of butyl iodide on the yield of butylated products (Bu-P) and benzene soluble products (BS): Yubari coal/dibutylzinc=1 g/7 g; reaction was carried out in a glass flask at 160 °C (bath temp).

However, a treatment with BuI and BuZnI was not very effective for coal solubilization. The yields of Bu-P and BS were 131 wt% and 51.2 wt%, respectively, when Yubari coal was treated with BuI (16 g) and BuZnI (5.8 g) at 130 °C for 5 h. These results strongly suggest that BuZnI, Bu_2Zn, and BuI are indispensable to attain high coal solubility in benzene.

Table 1. Yields of Butylated Products (Bu-P) and Benzene Soluble Products (BS) of Yubari Coal Treated with Either of Butylzinc Iodide (BuZnI) or Dibutylzinc (Bu_2Zn)

Butylzinc compound[a)]		Yield (wt%, daf)[b)] Bu-P	BS
BuZnI	15 ml	133	27.3
BuZnI	15 ml	142	35.7
BuZnI	35 ml	151	37.4
BuZnI	15 ml	140	34.6
Bu_2Zn	4 g	114	20.5
Bu_2Zn	7 g	134	26.7
Bu_2Zn	7 g	109	11.0
Bu_2Zn	10 g	130	28.5
Bu_2Zn	12 g	138	30.7
Bu_2Zn	15 g	140	37.1

a) BuZnI in THF (2.5 mol dm^{-3}) was used and reacted in an autoclave; Bu_2Zn was reacted in a glass flask. b) Bu-P and BS yields are based on the Yubari coal (daf) and Bu-P, respectively.

To determine the concentration of BuZnI in a mixture of BuZnI and Bu_2Zn solution, the supernatant solution cited in the preparation of butylzinc compounds was hydrolyzed. According to analyses of the amounts of butane which evolved, iodide and Zn, ca. 1 mol of BuZnI was found to dissolve in 0.8 mol of Bu_2Zn.[7] This solution showed similar ^1H and ^{13}C NMR spectra to those of Bu_2Zn (Table 2). Boersma and Noltes have reported that the ^1H NMR spectrum of a mixture of C_2H_5ZnX (X=Cl, Br, I) and $(C_2H_5)_2Zn$ in an aprotic non-polar solvent indicates only one set of ethyl group absorption, one triplet and one quartet. An exchange of ethyl groups between C_2H_5ZnX and $(C_2H_5)_2Zn$ occurs.[10] Therefore, a similar exchange of the butyl groups between BuZnI and Bu_2Zn is believed to occur in the mixture.

Effect of Chain Length of RX on BS Yield.

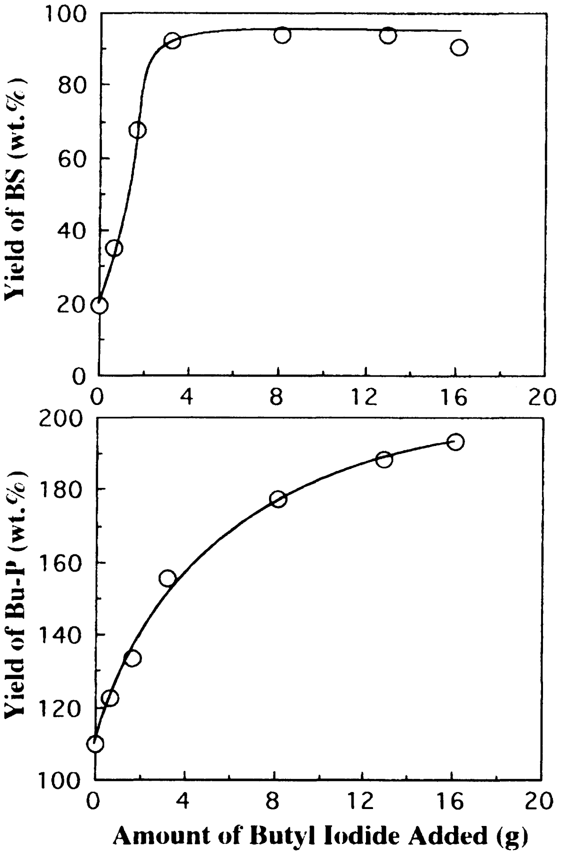

Fig. 2. Effect of addition of butyl iodide on the yields of Bu-P and BS: Yubari coal/BuZnI in Bu_2Zn=1 g/10 ml; reaction was carried out in a glass flask at 160 °C (bath temp).

Table 2. ^1H and ^{13}C NMR Spectral Data of Butylzinc Compounds[a)]

Compound	^1H NMR δ (ppm)	^{13}C NMR δ (ppm)
Bu_2Zn	0.40 (t, $ZnCH_2$)	14.1 (CH_3)
	0.91 (t, CH_3)	16.0 (CH_2Zn)
	1.31 (sextet, CH_2)	28.8 (CH_2)
	1.55 (quintet, CH_2)	29.5 (CH_2)
Mixture of BuZnI and Bu_2Zn	0.45 (t, $ZnCH_2$)	14.1 (CH_3)
	0.90 (t, CH_3)	16.1 (CH_2Zn)
	1.31 (sextet, CH_2)	28.9 (CH_2)
	1.54 (quintet, CH_2)	29.3 (CH_2)

a) Measured on a JEOL JNM-GSX400 spectrometer.

Usually in coal solubilization by alkylation, the solubility of the coal in the solvent increases along with an increase in the length of the alkyl groups.[11,12)] To investigate the effect of the chain length of the alkyl groups on coal solubilization, Yubari coal was treated with different kinds of alkyl halides (numbers of carbon=1—6) and BuZnI and/or Bu_2Zn. Figure 3 shows the relationship between the length of the alkyl groups introduced and the yields of the alkylated products and BS. Except for BS from the treatment with Bu_2Zn and ethyl iodide, all of the yields of BS were fairly high and the yield of the alkylated products increased along with an increase in the length of the alkyl groups. This upward tendency of the yield of the alkylated products indicates that the alkyl groups of the alkyl iodides are introduced into the coal. However, even an introduction of methyl groups was also effective for coal solubilization. In general, the introduction of methyl groups into coal is not so effective for high coal solubility in the case of reductive alkylation.[11,12)] We therefore expect that not only the alkyl groups of alkyl halides, but also the butyl groups of Bu_2Zn or BuZnI are introduced into the coal.

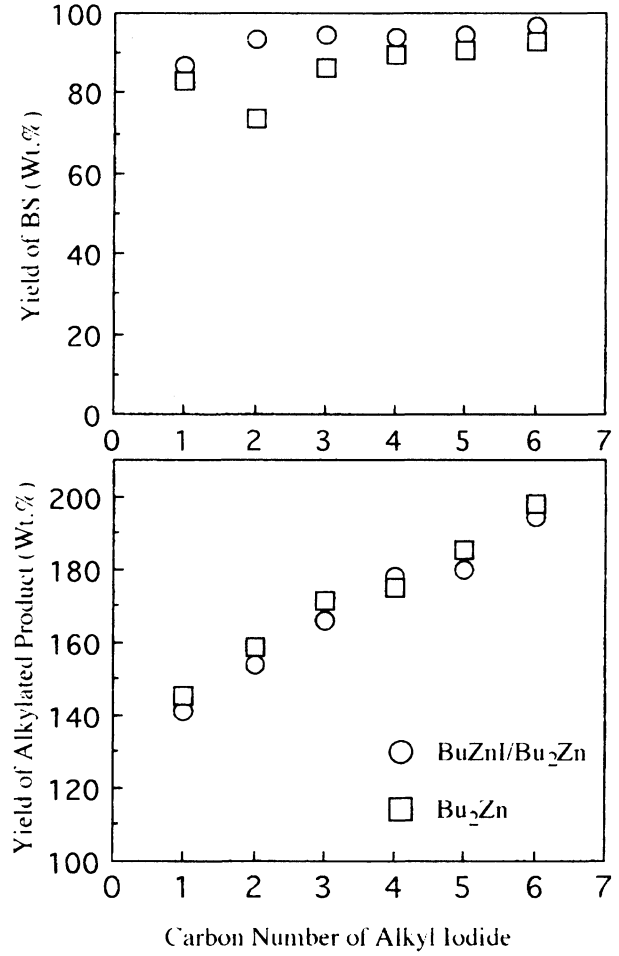

Fig. 3. Relation between the yield of BS and the chain length of alkyl halide: Reaction was carried out in a glass flask.

To determine which alkyl groups are introduced into coal, Yubari coal was treated with ^{13}C-enriched methyl iodide ($^{13}CH_3I$) and a mixture of BuZnI and Bu_2Zn; the ^{13}C NMR spectrum of BS was then examined. Figure 4 shows the ^{13}C NMR spectrum of the resulting BS. For a comparison, the ^{13}C NMR spectra of the BS of Bu-P treated with CH_3I or BuI under otherwise the same conditions are also shown. Because the intense peaks at 14.0 and 22.9 ppm in the spectra of BS treated with CH_3I are due to C_δ and C_γ of the introduced

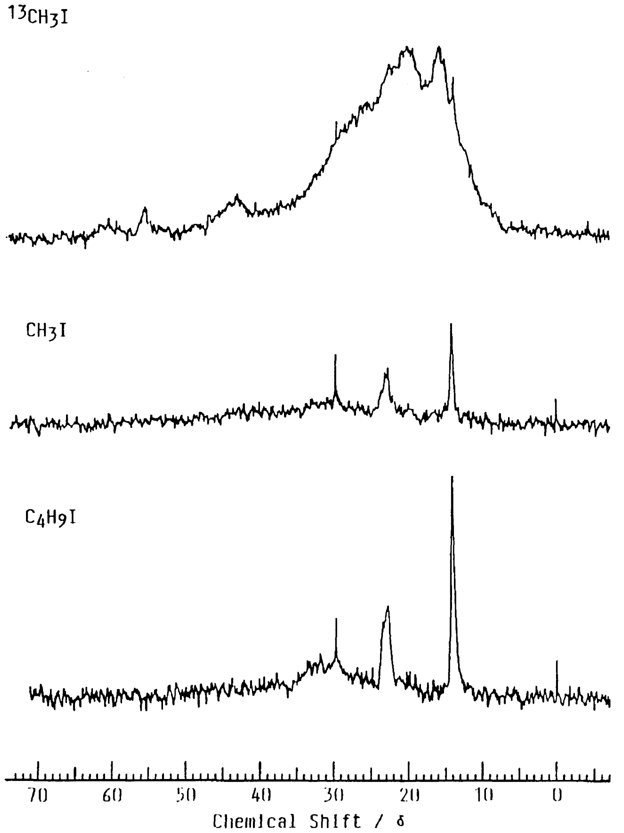

Fig. 4. ^{13}C NMR spectra of the BS of Bu-P treated with $^{13}CH_3I$, CH_3I, or BuI and BuZnI in the presence of Bu_2Zn.

Table 3. Effect of Addition of BuX on the Coal Solubilization[a)]

Butylzinc compound		BuX added		Yield (wt%,daf)[c)]	
	g		g	Bu-P	BS
Bu_2Zn	10	BuCl	4.0	144	48.8
$BuZnCl/Bu_2Zn$[b)]	12	BuCl	4.0	133	73.3
Bu_2Zn	10	BuBr	6.0	132	50.6
$BuZnBr/Bu_2Zn$[b)]	12	BuBr	6.0	155	96.1
Bu_2Zn	10	BuI	8.0	185	87.7
$BuZnI/Bu_2Zn$[b)]	11	BuI	8.0	178	93.8

a) Yubari coal (1 g) was treated in a glass flask for 5 h under reflux. b) BuZnX was used in a saturated solution of Bu_2Zn. c) Yields of Bu-P and BS are based on the Yubari coal and Bu-P, respectively.

butyl groups,[13)] it is clear that both the methyl and butyl groups are introduced concurrently. The band from 22 to 30 ppm of the spectrum of the BS treated with $^{13}CH_3I$ was a characteristic for the methyl groups reductively introduced to aromatic moieties, while the band at the lower chemical shift (10—22 ppm) could be attributed to substituted methyl groups of the aromatic rings.[13—15)] Both the substitution and addition of methyl groups to aromatic moieties of coal occurred, this also being parallel with the results of a study of model compounds of coal structures in the Zn/BuI system.[3)]

Effect of the Halogen Atom in Both BuX and BuZnX on the BS Yield. To examine the effectiveness of different halogens in BuZnX (X=Cl, Br, I) and BuX (X=Cl, Br, I) for coal solubilization, Yubari coal was treated with BuZnX (X=Cl, Br, I) and/or Bu_2Zn in the presence of BuX (X=Cl, Br, I). Table 3 shows the yields of Bu-P and BS. The benzene solubilities of Bu-P treated with Bu_2Zn, and either BuCl or BuBr were low. Their BS yields were about 50 wt%. However, a treatment with a mixture of BuZnX (X=Cl, Br) and Bu_2Zn in the presence of BuX (X=Cl, Br) was effective for coal solubilization. These findings suggest that BuZnX (X=Cl, Br) plays a significant role in increasing coal solubilization. The fact that a treatment with a mixture of BuZnI, Bu_2Zn, and BuI was found to be more effective for coal solubilization than those with Bu_2Zn and BuI, agrees with the case described above (X=Cl, Br). Therefore, treating coal with Bu_2Zn and either of BuCl or BuBr is considered not to be so effective for coal solubilization, because the amount of BuZnCl or BuZnBr formed was low. All of the yields of BS obtained from treatments with a mixture of BuZnX, Bu_2Zn, and BuX were over 73%, irrespective of the kind of halogen of BuZnX and BuX.

Mechanism of Coal Solubilization. As shown in Table 3, a mixture of BuZnX, Bu_2Zn, and BuX (X=Cl, Br, I) was more effective for coal solubilization than those of Bu_2Zn and BuX (X=Cl, Br, I), although the amounts of butyl groups introduced were smaller in the case of a mixture of BuZnX (X=Cl, I), Bu_2Zn, and BuX (X=Cl, I) than those of Bu_2Zn and BuX (X=Cl, I).

We have already reported that both Friedel–Crafts-type and radical-type butylation occurred competitively in the Zn/BuI system. Both the butyl-substitution and butyl-addition products were formed by a Friedel–Crafts-type and a radical-type butylation, respectively.[3)] Usually, butyl-addition reactions are much more effective for coal solubilization than are butyl-substitution reactions in the solubilization of coal by alkylation.[12)] The effect of the amounts of butyl groups on the BS yields was examined by referring to treatments with BuZuI and/or Bu_2Zn in the presence of BuI. Figure 5 shows a relation between the BS yields and the number of butyl groups introduced into 100 carbon atoms. The number of butyl groups was calculated based on the changes in the H/C ratio, carbon balance and material balance, the mean value of three numbers being adopted. When many butyl groups were introduced into Bu-P, the BS yields from both reactions were almost the same. However, when the number of butyl groups introduced into Bu-P was about 12, the BS yield with a mixture of BuZnI, Bu_2Zn, and BuI was higher than that with Bu_2Zn and BuI. We therefore believe that in the beginning of the reaction with Bu_2Zn and BuI, Friedel–Crafts-type butylation is dominant, according to Eqs. 2 and 3, and that the radical-type

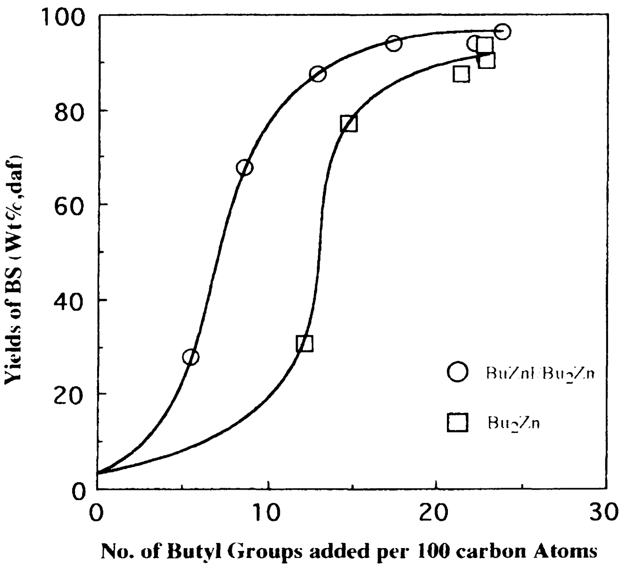

Fig. 5. Relation between the yield of BS and the butyl groups introduced into 100 carbon atoms of Bu-P: Reaction was carried out in a glass flask.

butylation is gradually replacing it, due to increasing amounts of BuZnI formed Eqs. 2, 3, and 4. In a reaction with a mixture of BuZnI, Bu_2Zn, and BuI, a radical-type butyl-addition is expected to take place predominantly.[16)]

To confirm the occurrence of radical-type butylation, the FT-IR spectra of two Bu-P from both treatments with a mixture of BuZnI, Bu_2Zn, and BuI, and that of Bu_2Zn and BuI were measured. Figure 6 shows the IR spectra of these two Bu-P, as well as their difference spectrum. Both Bu-P samples were selected in such a way as to have almost the same number (ca. 12) of butyl groups introduced. However, there was a significant difference in the BS yields (91 wt% for the case of the mixture of BuZnI, Bu_2Zn, and BuI, and 31 wt% for that of Bu_2Zn and BuI, see Fig. 5). It was expected that the IR spectrum of the Bu-P from a treatment with a mixture of BuZnI, Bu_2Zn, and BuI showed a lower intense band of C=C stretching (about 1600 cm^{-1}) in aromatic nuclei and a higher intense band at methyn stretching at about 2890 cm^{-1} than the corresponding bands of the Bu-P from that with Bu_2Zn and BuI. Their difference spectrum showed a clearly intense negative band of C=C stretching of aromatic nuclei at 1600 cm^{-1}, and a positive peak of methyn CH stretching at 2959 cm^{-1}. From these results, it was concluded that the butyl-addition reaction prevails in a treatment of coal with a mixture of BuZnI, Bu_2Zn, and BuI. A treatment with a mixture of BuZnI, Bu_2Zn, and BuI was more effective for coal solubilization than that with Bu_2Zn and BuI.

Conclusion. The solubility of coal in benzene was found to be accelerated by a treatment of coal with Bu_2Zn and/or BuZnX (X: Cl, Br, I) in the presence of BuX. A spectral study on each Bu-P from two runs of coal solubilization in Bu_2Zn/BuZnI/BuI and Bu_2Zn/BuI systems suggested that the addition reaction of alkyl groups to aromatic moieties of coal prevails in the former system than a substitution reaction. In these systems, the addition reaction was found to be more effective in increasing the solubility of coal in a solvent than a substitution reaction. For coal solubilization in the Bu_2Zn/BuI system, Bu_2Zn, BuZnI, and BuI are evaluated to be indispensable active species.

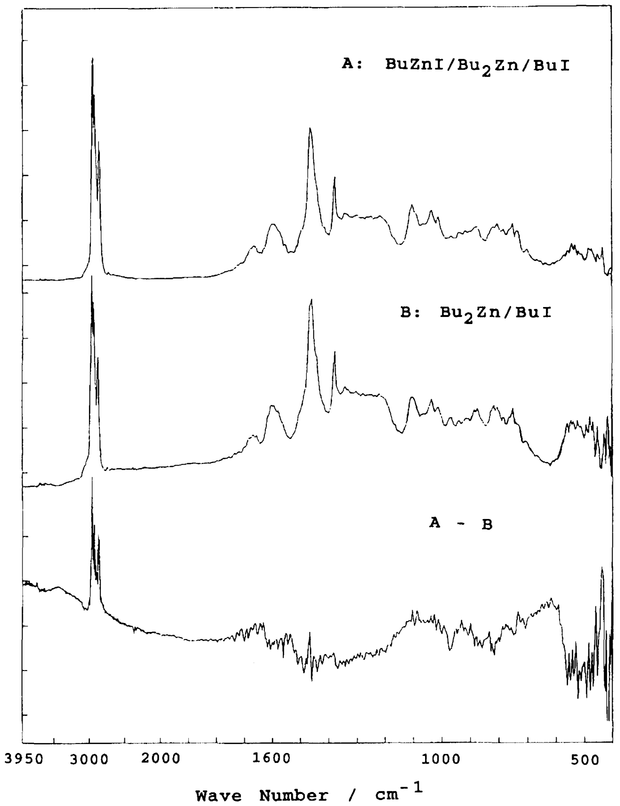

Fig. 6. FT-IR spectra of the Bu-P and their difference spectrum.

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