

## Active Species in Zn-Butyl Iodide System for Coal Solubilization

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Yubari coal treated with supernatant solution formed from a reaction of  $\text{Bu}_2\text{Zn}$  and  $\text{ZnI}_2$  in the presence of butyl iodide shows 97 wt% of solubility in benzene, which is comparable with that obtained from one treated in a zinc-butyl iodide system. This result suggests that dibutylzinc, butylzinc iodide, and butyl iodide are indispensable species in the zinc-butyl iodide system for coal solubilization.

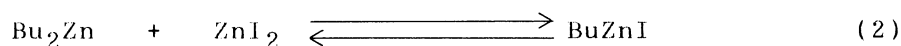
When treated with zinc and butyl iodide at 130 °C under atmospheric pressure, coals become extensively soluble in benzene.<sup>1,2)</sup> Although we previously proposed that Friedel-Crafts type and radical type alkylations occur competitively in the reaction,<sup>3)</sup> coals treated with butyl iodide in the presence of  $\text{AlCl}_3$ <sup>1,4)</sup> or  $\text{ZnI}_2$ <sup>5)</sup> have also been found to solubilize in benzene, though in a small extent. However the reaction conditions used in a Zn-butyl iodide system are fairly similar to those for the preparation of both butylzinc iodide ( $\text{BuZnI}$ ) and dibutylzinc ( $\text{Bu}_2\text{Zn}$ ).<sup>6,7)</sup> Therefore these organozinc compounds seem to be formed *in situ* in the Zn-butyl iodide system. In order to clarify the active species in this Zn-butyl iodide system, both butylzinc compounds have been examined as probable reagents to solubilize coals effectively.

Yubari coal was grounded to 100 mesh under and dried to constant weight at 60 °C under vacuum. The analytical data were reported previously.<sup>1,2)</sup> Both  $\text{Bu}_2\text{Zn}$  and  $\text{BuZnI}$  were prepared according to the reported methods<sup>6-8)</sup> and operated under dry nitrogen atmosphere;  $\text{Bu}_2\text{Zn}$ : bp 34 -35 °C/1 mmHg.  $\text{BuZnI}$  was used in tetrahydrofuran (THF; 2.5 mol  $\text{dm}^{-3}$ ). Butylation was carried out as follows: Yubari coal (1 g) and  $\text{Bu}_2\text{Zn}$  (1 g) or  $\text{BuZnI}$  (2.5 mol  $\text{dm}^{-3}$ ; 15ml) in the presence or the absence of butyl iodide ( $\text{BuI}$ ) were placed either in a 100 ml teardrop type flask or a 100 ml autoclave. The mixture was stirred at 130 - 180 °C for a given period and then poured into water. The product was washed with dilute hydrochloric acid and hot water until no halogen ion was detected. A benzene-soluble product (BS) was obtained by benzene extraction at 60 °C. Yields (wt%,

daf) of the butylated products (Bu-P) and BS were estimated by drying the solid products to constant weight at 60 °C under vacuum. Solubility efficiency (Es), which suggests the degree of effectiveness of added butyl groups on solubilization, was calculated by Eq.1.<sup>2)</sup> The analytical methods were described previously.

$$Es = \frac{Bu-P \text{ Yield (wt\%)} \times BS \text{ Yield (wt\%)} / 100}{Bu-P \text{ Yield (wt\%)} - 100} \quad (1)$$

BuZnI and Bu<sub>2</sub>Zn in THF are in the equilibrium which can be regarded as Schlenk one (Eq.2). Because the equilibrium lies far on the side of



BuZnI,<sup>9)</sup> BuZnI in THF was used in the present study. Since BuI seems to exist with both Bu<sub>2</sub>Zn and BuZnI in a zinc-butyl iodide system, additive effect of BuI on solubilization was also examined. Results of coal solubilization using either Bu<sub>2</sub>Zn or BuZnI are shown in Table 1. The

Table 1. Butylation of Yubari Coal with Butylzinc Compounds

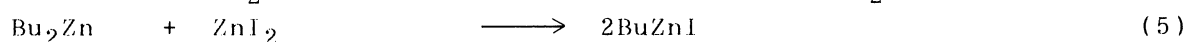
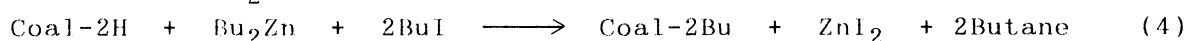
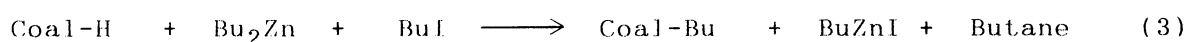
Butylzinc compound <sup>a)</sup>		BuI added /ml	Reaction temp/° C	Reaction time /h	Yield (wt%) Bu-P <sup>b)</sup> BS <sup>c)</sup>		Es <sup>d)</sup>
BuZnI	15ml	0	140	6.0	133	27.3	1.10
BuZnI	15ml	0	140	6.0	142	35.7	1.21
BuZnI	35ml	0	140	6.0	151	37.4	1.11
BuZnI	15ml	0	130	5.0	140	34.6	1.21
BuZnI	15ml	5.0	130	5.0	153	48.3	1.39
BuZnI	15ml	10.0	130	5.0	144	35.9	1.19
Bu <sub>2</sub> Zn	4g	0	180	2.2	114	20.5	1.67
Bu <sub>2</sub> Zn	7g	0	180	2.2	134	26.7	1.05
Bu <sub>2</sub> Zn	10g	0	180	2.3	130	28.5	1.24
Bu <sub>2</sub> Zn	12g	0	180	2.7	138	30.7	1.11
Bu <sub>2</sub> Zn	15g	0	180	2.7	140	37.1	1.03
Bu <sub>2</sub> Zn	7g	0	130	5.0	109	11.0	1.33
Bu <sub>2</sub> Zn	7g	5.0	130	5.0	159	48.0	1.29
Bu <sub>2</sub> Zn	7g	7.5	130	5.0	196	77.6	1.58
Bu <sub>2</sub> Zn	7g	10.0	130	5.0	199	83.9	1.69

a) BuZnI in THF (2.5 mol dm<sup>-3</sup>) was used. b, c) Yields are based on original coal and butylated products (Bu-P), respectively.

d) Solubilization efficiency.

treatment using only one of butylzinc compounds ( $\text{Bu}_2\text{Zn}$  or  $\text{BuZnI}$ ) was not so effective;<sup>10)</sup> addition of  $\text{BuI}$  for  $\text{BuZnI}$  was not effective for coal solubilization, either. In the case of  $\text{Bu}_2\text{Zn}$ , however, addition of  $\text{BuI}$  was very effective for coal solubilization. With increase of the amount of  $\text{BuI}$ , yields of Bu-P and BS gradually increased to 199 wt% and 83.9 wt%, respectively, which are comparable to those attained in Zn-butyl iodide system.

Although the combination of  $\text{BuZnI}$  in THF and  $\text{BuI}$  exhibited an effect on coal solubilization, though a little,  $\text{BuZnI}$  seems to be produced in the reaction of coal with  $\text{Bu}_2\text{Zn}$  and  $\text{BuI}$  (Eqs.3-5).<sup>11,12)</sup> To confirm the



effectiveness of additive  $\text{BuZnI}$ , Yubari coal was also treated with a supernatant solution,<sup>13)</sup> which was made from a reaction of  $\text{Bu}_2\text{Zn}$  and excess  $\text{ZnI}_2$  at 70 °C,<sup>12)</sup> in the presence or in the absence of added  $\text{BuI}$ . Although the supernatant itself had a little effect on coal solubilization, addition of  $\text{BuI}$  was found to be excellently effective as shown in Table 2. The solubility (97 wt%) is higher than all of those attained from Yubari coal treated with zinc and butyl iodide. These results clearly indicate that

Table 2. Butylation of Yubari Coal with Supernatant<sup>a)</sup> and  $\text{BuI}$ <sup>b)</sup>

Supernatant (ml)	$\text{BuI}$ added (ml)	Yield (wt%)		$\text{Es}^{\text{e)}$
		Bu-P <sup>c)</sup>	BS <sup>d)</sup>	
9.6	0	114	18.1	1.47
10.2	0	110	19.0	2.09
5.6	8	201	94.4	1.88
7.5	11	190	96.5	2.04

a) Supernatant was prepared with  $\text{Bu}_2\text{Zn}$  (13.3ml) and excess  $\text{ZnI}_2$  (12.3g) at 70 °C for 2 h. b) Reactions were carried out by using Yubari coal (1 g) at 130 °C under atmospheric pressure for 5 h. c, d) Yields are based on original coal and butylated products (Bu-P), respectively.

e) Solubilization efficiency.

both BuI and the mixture composed of Bu<sub>2</sub>Zn and BuZnI exerted a significant effect on coal solubilization.

Since the reagents for preparations of Bu<sub>2</sub>Zn and BuZnI are similar to those in the Zn-butyl iodide system as well as the reaction conditions and yet a mixture of Bu<sub>2</sub>Zn, BuZnI, and BuI is very effective for coal solubilization, it is concluded that these three reagents are substantially effective species for coal solubilization in the Zn-butyl iodide system.

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- 5) Yields (daf) of Bu-P and BS of Yubari coal (1.5 g) treated with BuI (15 ml) and ZnI<sub>2</sub> (16 g) at 130 °C for 5 h were 109 wt% and 5.7 wt%, respectively.
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- 10) BS for BuZnI in THF were contaminated with a small amount of decomposed products from THF; D. B. Smith and A. C. Skinner, *J. Chem. Soc.*, **1963**, 577.
- 11) Butane was detected in the gases evolved during the reaction of coal with Bu<sub>2</sub>Zn and BuI.
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- 13) The supernatant is composed of about 1.8 mol ratio of zinc, 1 mol ratio of iodide, and 2.4 mol ratio of butyl group, showing similar <sup>1</sup>H and <sup>13</sup>C NMR spectra to those of Bu<sub>2</sub>Zn.

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