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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 Bu_2Zn and 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.[1,2] Although we previously proposed that Friedel-Crafts type and radical type alkylations occur competitively in the reaction,[3] coals treated with butyl iodide in the presence of $AlCl_3$[1,4] or ZnI_2[5] 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 (BuZnI) and dibutylzinc (Bu_2Zn).[6,7] 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.[1,2] Both Bu_2Zn and BuZnI were prepared according to the reported methods[6-8] and operated under dry nitrogen atmosphere; Bu_2Zn: bp 34 -35 °C/1 mmHg. BuZnI was used in tetrahydrofuran (THF; 2.5 mol dm^{-3}). Butylation was carried out as follows: Yubari coal (1 g) and Bu_2Zn (1 g) or BuZnI (2.5 mol dm^{-3}; 15ml) in the presence or the absence of butyl iodide (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.[2] The analytical methods were described previously.

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

BuZnI and Bu_2Zn in THF are in the equilibrium which can be regarded as Schlenk one (Eq.2). Because the equilibrium lies far on the side of

$$Bu_2Zn + ZnI_2 \rightleftharpoons BuZnI \quad (2)$$

BuZnI,[9] BuZnI in THF was used in the present study. Since BuI seems to exist with both Bu_2Zn and BuZnI in a zinc-butyl iodide system, additive effect of BuI on solubilization was also examined. Results of coal solubilization using either Bu_2Zn or BuZnI are shown in Table 1. The

Table 1. Butylation of Yubari Coal with Butylzinc Compounds

Butylzinc compound[a]	BuI added /ml	Reaction temp/°C	Reaction time /h	Yield (wt%) Bu-P[b]	Yield (wt%) BS[c]	Es[d]
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_2Zn 4g	0	180	2.2	114	20.5	1.67
Bu_2Zn 7g	0	180	2.2	134	26.7	1.05
Bu_2Zn 10g	0	180	2.3	130	28.5	1.24
Bu_2Zn 12g	0	180	2.7	138	30.7	1.11
Bu_2Zn 15g	0	180	2.7	140	37.1	1.03
Bu_2Zn 7g	0	130	5.0	109	11.0	1.33
Bu_2Zn 7g	5.0	130	5.0	159	48.0	1.29
Bu_2Zn 7g	7.5	130	5.0	196	77.6	1.58
Bu_2Zn 7g	10.0	130	5.0	199	83.9	1.69

a) BuZnI in THF (2.5 mol dm^{-3}) 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 (Bu_2Zn or BuZnI) was not so effective;[10] addition of BuI for BuZnI was not effective for coal solubilization, either. In the case of Bu_2Zn, however, addition of BuI was very effective for coal solubilization. With increase of the amount of 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 BuZnI in THF and BuI exhibited an effect on coal solubilization, though a little, BuZnI seems to be produced in the reaction of coal with Bu_2Zn and BuI (Eqs.3-5).[11,12] To confirm the

$$\text{Coal-H} + Bu_2Zn + \text{BuI} \longrightarrow \text{Coal-Bu} + \text{BuZnI} + \text{Butane} \quad (3)$$

$$\text{Coal-2H} + Bu_2Zn + 2\text{BuI} \longrightarrow \text{Coal-2Bu} + ZnI_2 + 2\text{Butane} \quad (4)$$

$$Bu_2Zn + ZnI_2 \longrightarrow 2\text{BuZnI} \quad (5)$$

effectiveness of additive BuZnI, Yubari coal was also treated with a supernatant solution,[13] which was made from a reaction of Bu_2Zn and excess ZnI_2 at 70 °C,[12] in the presence or in the absence of added BuI. Although the supernatant itself had a little effect on coal solubilization, addition of 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[a] and BuI[b]

Supernatant (ml)	BuI added (ml)	Yield (wt%) Bu-P[c]	BS[d]	Es[e]
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 Bu_2Zn (13.3ml) and excess 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_2Zn and BuZnI exerted a significant effect on coal solubilization.

Since the reagents for preparations of Bu_2Zn and BuZnI are similar to those in the Zn-butyl iodide system as well as the reaction conditions and yet a mixture of Bu_2Zn, 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.

References

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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_2Zn 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 ^{1}H and ^{13}C NMR spectra to those of Bu_2Zn.

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