

THE EFFECT OF SOLVENT ON THERMAL CRACKING OF BIBENZYL
AS A COAL MODEL

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The effect of solvent on bibenzyl conversion depends on the nature of solvent. Triphenylmethane, diphenylmethane, and diphenylamine are poor hydrogen donor solvents. But, when these compounds were used as solvent, bibenzyl conversion was markedly enhanced, and toluene, stilbene and adducts were formed. Moreover, when a proper amount of tetralin was mixed with the above solvent, toluene was solely obtained in reasonable yield.

There has been renewed recent interest in thermal cracking of bibenzyl,¹⁻⁵⁾ which serves as the simplest model for dimethylene connecting units in coal. But, these interests were mainly in thermal cracking of bibenzyl in good hydrogen donor solvents.

Cronauer et al.⁶⁾ reported the mechanism and kinetics of reactions between bibenzyl and a few of non-hydrogen donor or hydrogen donor solvents. The major conclusion of their study was that the breakage of the carbon-carbon bond in bibenzyl occurs purely thermally and its rate is independent of the nature of the solvent present during reaction. However, a detailed discussion of the reactions taking place between bibenzyl and a variety of non-hydrogen donor solvents have not been published.

We have recently found that thermal cracking of bibenzyl was significantly promoted by using triphenylmethane, diphenylmethane, or diphenylamine as solvent. These solvents have poor hydrogen donating ability as described later.

It has been accepted that the hydrogen donating ability of solvent plays the most important role in the scission of methylene linkage presumed to be present in coal. However, the informations derived from the present letter suggest that part of poor hydrogen donor solvents are able to play more significant role than good hydrogen donor solvents.

Experiments were performed in a 100 ml magne-driven autoclave. The autoclave charged with bibenzyl (1.00 g) and solvent (20.00 g) was filled with nitrogen at an initial pressure of 3 MPa, and then was heated at 400 or 450 °C for 1 h. After cooling, the content of the reactor was taken out with acetone. The acetone solution was analyzed with GC using silicone grease DC 550 (20%) / Cellite 545 (60-80 mesh) 4 mmφ x 2 m column. The results are summarized in Table 1. Toluene and stilbene yields (mol%) in Table 1 were calculated on the basis of bibenzyl used. And adducts (mol%) were calculated according to the following equation,

Table 1. Thermal cracking of bibenzyl^{a)} (1)

Solvent	Reaction temp /°C	Conversion of bibenzyl/%	Products ^{b)} (mol%)		
			Toluene	Stilbene	Adduct ^{c)}
1,2,3,5-Tetramethylbenzene	450	22.0	17.9	0.0	4.1
1,4-Diisopropylbenzene	450	25.5	25.6	0.0	0.0
Tetralin	450	40.3	40.0	0.0	0.3
9,10-Dihydroanthracene	450	43.0	38.6	trace	4.4
Diphenylmethane	450	61.0	42.3	12.4	6.3
Triphenylmethane	450	62.8	37.0	5.4	20.4
Diphenylamine	450	57.3	42.4	1.2	13.7
Tetralin	400	6.4	1.7	0.0	4.7
Diphenylmethane	400	10.6	3.8	1.9	4.9
Triphenylmethane	400	12.0	2.0	0.0	10.0

a) Bibenzyl (1.00 g) and solvent (20.00 g) were used in each reaction. The reactions were carried out at 400 or 450 °C for 1 h under nitrogen pressure (3 MPa at room temp).

b) The yields were calculated on the basis of bibenzyl used.

c) Adduct (mol%) = bibenzyl conversion (%) - toluene (mol%) - stilbene (mol%)

Table 2. Thermal cracking of bibenzyl^{a)} (2)

Solvent (weight ratio)	Conversion of bibenzyl/%	Products ^{b)} (mol%)		
		Toluene	Stilbene	Adduct ^{c)}
Tetralin	40.3	40.0	0.0	0.3
Tetralin - Triphenylmethane (1 : 3)	62.6	62.7 ^{d)}	0.0	-
" (1 : 1)	50.2	51.2 ^{d)}	trace	-
" (3 : 1)	48.9	50.2 ^{d)}	0.0	-
Tetralin - Diphenylmethane (1 : 3)	52.2	53.3 ^{d)}	trace	-
" (1 : 1)	43.1	43.4 ^{d)}	trace	-
" (3 : 1)	39.8	40.3 ^{d)}	trace	-

a) Bibenzyl (1.00 g) and solvent (20.00 g) were used in each reaction. The reactions were carried out at 450 °C for 1 h under nitrogen pressure (3 MPa at room temp).

b), c) The same as in Table 1.

d) Toluene yield appears to pass over bibenzyl conversion by experimental error.

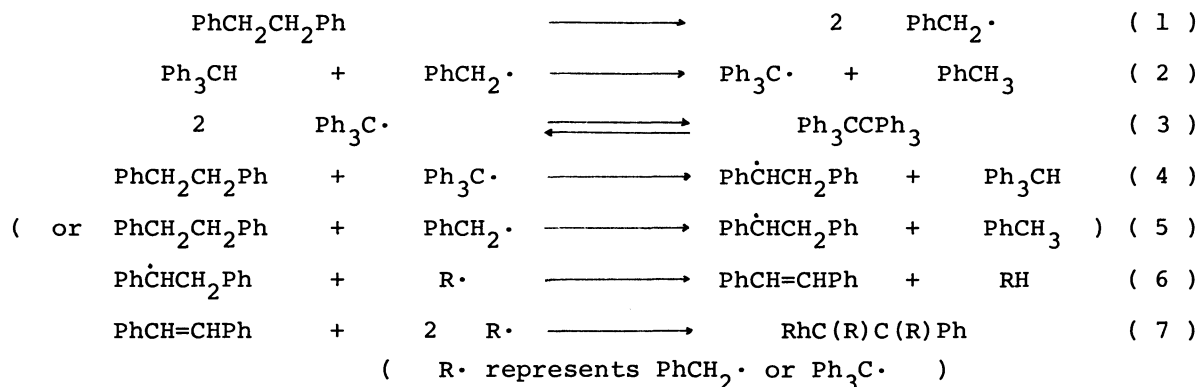
and hence these values also include the products other than the adduct formed by combination of Bibenzyl with solvent.

Adduct (mol%) = bibenzyl conversion (%) - toluene (mol%) - stilbene (mol%)

As Cronauer et al.⁶⁾ noticed, bibenzyl conversion obtained using tetralin was close that when using 9,10-dihydroanthracene thought to be more active donor. But, when other solvents were used at 450 °C, bibenzyl conversions varied widely from 22.0 to 62.8%, and also the products distributions were various. When diphenylmethane, triphenylmethane, and diphenylamine were used, bibenzyl conversions were markedly enhanced especially at 450 °C, and toluene, stilbene and adduct were formed. These results are interesting, for those solvents is able to form stable radicals such as triphenylmethyl, diphenylmethyl, and diphenylamino radicals, and indicate that the effect of solvent on bibenzyl conversion depends on the nature of solvent. The products obtained using triphenylmethane at 450 °C were isolated by column chromatography on alumina, and a large amount of toluene, a lesser amount of stilbene, small amounts of phenanthrene, 9-phenylfluorene and unknown high molecular products, and a very small amount of 1,1,1,2-tetraphenylethane were obtained. These were respectively identified by comparing the retention times in GC, ¹H-NMR and IR spectra with those of the authentic samples.

Phenanthrene and 9-phenylfluorene must be formed by dehydrogenation from stilbene and triphenylmethane respectively.

From these results, the following main reaction route was assumed.



As triphenylmethane is more stable than bibenzyl,⁷⁾ triphenylmethane will not be directly decomposed into triphenylmethyl radical, and so the radical appears to be formed by attack of benzyl radical on triphenylmethane.

In the similar manner, thermal cracking of bibenzyl appears to be promoted also by diphenylmethyl and diphenylamino radicals. The stable radicals such as triphenylmethyl, diphenylmethyl, diphenylamino and so on may have the large effect in this thermal cracking. These radicals may be formed by attack of benzyl radical on the parent solvents as above mentioned, and the reactions can be initiated only when the methylene linkage in bibenzyl is thermally severed.

According to the procedure described by Yokono et al.,⁸⁾ hydrogen donating ability of the solvents were estimated by the extent of hydrogen transfer from the solvents to anthracene. When a mixture of anthracene and an equal weight of tetralin was heated at 400 °C for 1 h, the yield of 9,10-dihydroanthracene was 56%. But, when a mixture of anthracene and triphenylmethane, diphenylmethane or diphenylamine

was treated under the similar conditions, the yield of 9,10-dihydroanthracene was trace. The above results indicated that these solvents are poor hydrogen donor, and the effectiveness of these solvents in this reaction are not directly related to the hydrogen donating ability.

On the other hand, as shown in Table 2, when a proper amount of tetralin was mixed with triphenylmethane or diphenylmethane, toluene was obtained in reasonable yield, and stilbene and adduct were scarcely formed. But bibenzyl conversion and toluene yield decreased gradually with increasing amount of tetralin.

In addition, stilbene (1.00 g) and tetralin (20.00 g) were heated under the similar conditions. Conversion of stilbene was 94.5%, and yields of toluene and bibenzyl were 37.0 and 55.1% respectively.

When a proper amount of tetralin is mixed with triphenylmethane or diphenylmethane, stilbene formed during reaction may be converted into toluene and bibenzyl. But, if a large amount of tetralin is added, triphenylmethyl radical may be hydrogenated by tetralin and bibenzyl conversion decrease.

Further, it is believed that most of tetralin is in liquid state under coal liquefaction conditions.⁹⁾ As other solvents in the present letter have higher boiling points than tetralin, the reactions appear to proceed mainly in liquid phase.

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