

Modelling the Thermal Reactions of Benzyl Phenyl Sulfide

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The reactions of benzylphenylsulfide (BPS) neat, in benzene, in tetralin and with added thiophenol were studied. A free-radical mechanism described the neat pyrolysis of BPS to the major products toluene, thiophenol, diphenyldisulfide, and diphenylsulfide. An analytical rate expression deduced from this mechanism was consistent with results from both neat pyrolysis and reaction with additives. The secondary reactions of primary products were detailed.

Our interest in the resolution of reaction fundamentals in supercritical fluid (SCF) solvents has motivated careful study of the thermolysis pathways, kinetics and mechanisms that will generally occur in parallel with any possible solvolysis. Since reactions with a SCF solvent of compounds containing oxygen (Lawson and Klein, 1985; Townsend and Klein, 1985) and nitrogen (Abraham and Klein, 1985; Tiffany, et al., 1984), but not sulfur, have been reported, our interest extended to the reactions of benzylphenylsulfide (BPS). Herein we report on a mathematical model of BPS pyrolysis that is based on our own experiments and also the literature base on which our work is built.

Previous studies suggest that neat pyrolysis of BPS proceeds by a free-radical mechanism (Attar, 1978). The mechanism likely involves fragmentation of the C-S bond to a free-radical pair followed by stabilization through hydrogen abstraction, from either a hydrogen donor source, such as tetralin, or other hydrocarbon molecules in the reaction mixture. Fixari and coworkers (1984) pyrolysed BPS in benzene and in tetralin. For reaction in benzene, they postulated that BPS cleaved to a benzyl-phenylthiyl radical pair, which stabilized primarily by recombination. For reaction in tetralin, hydrogen abstraction was from tetralin, which led to a tetralyl radical intermediate whose disproportionation ultimately led to naphthalene. Huang and Stock (1982) also describe a free-radical mechanism for BPS decomposition. Thus the literature provides a good foundation from which to model the reaction of BPS.

Our investigation into the reactions of BPS addressed its neat pyrolysis first. Special attention was paid to derivative experiments, used in a detailed probe of the mechanism, which included reaction in the hydrogen-donor

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solvent tetralin, reaction in the inert solvent benzene, reaction with the addition of thiophenol, and the pyrolysis of diphenyldisulfide. This provided a basis with which to summarize the experimental results in terms of plausible reaction pathways and a reaction model.

EXPERIMENTAL

The reactants, solvents, and GC standards were all commercially available and used as received. A typical experimental procedure was as follows: the reactants, solvent, and the demonstrably inert (Townsend and Klein, 1985) internal standard biphenyl were loaded into batch "tubing bomb" reactors comprising one Swagelok port connector and two caps of 1/4" nominally sized stainless steel parts. The tubing bombs were sealed and immersed in a constant temperature sandbath. In approximately two min, the reactors reached the nominal reaction temperature and, after the desired time had passed, reactions were quenched by insertion of the reactor into a cold water bath. A representative initial concentration of BPS was 0.5 mol/L.

Spectrophotometric-grade acetone or reagent-grade tetrahydrofuran was used to collect all material from the reactors in one phase. Product identification was accomplished on an HP 5970 series GC/MSD equipped with a 60m DB-5 fused-silica capillary column. Quantitation of individual product yields was by GC using an HP 5880 instrument with the same type of capillary column and a flame ionization detector. Response factors were estimated from analyses of standard mixtures, which allowed quantitative calculation of product yields and, hence, an observed product index (OPI). This was the sum of the mass of identified GC-elutable products divided by the initial mass of reactant charged.

RESULTS

The reactions of benzylphenylsulfide (BPS) with a set of coreactants complemented the study of its neat pyrolysis and allowed a deeper probe of operative pathways and mechanisms. Reaction in the hydrogen-donor solvent tetralin highlighted unimolecular fission steps, whereas reaction in benzene allowed determination of the overall reaction order. Experiments with added thiophenol probed a major non-primary pathway, and the secondary reaction of diphenyldisulfide (DPDS) was investigated through its neat pyrolysis. The experimental conditions and major products are summarized in Table 1.

The presentation of the results is organized into sections that describe, respectively, neat pyrolysis and the derivative copyrolysis experiments. Within each section, the identity of all products and the temporal variation of the yields ($y_i = n_i/n_{\text{BPS}_0}$) of major products are presented first. This is followed by examination of product selectivity (y_i/x) and the effect of the loading of additive i ($S_i = n_{i0}/n_{\text{BPS}_0}$). Likely pathways and their kinetics are presented in the discussion.

Neat pyrolysis. Toluene was the major product of the neat pyrolysis of BPS. Other major products were DPDS, diphenylsulfide (DPS), and thiophenol; diphenylmethane and bibenzyl were minor products. The temporal variations of the yields of major products from pyrolysis at 300°C are shown in Figure 1, which indicates, by their initially positive associated slopes, that toluene, DPDS and thiophenol were primary products. OPI was greater than 0.9 at a BPS

conversion $x = 0.9$, which occurred after 120 min. The pseudo-first order rate constants and associated Arrhenius parameters for the disappearance of BPS during neat pyrolysis are summarized in Table 2.

Reaction in tetralin. Thermolysis of BPS in tetralin led to toluene and thiophenol as major products along with minor amounts of diphenylmethane and DPDS. The temporal variations of the yields of the major products from thermolysis at 340°C are shown in Figure 2, which indicates, by their initially positive slopes, that both toluene and thiophenol were primary products. OPI remained above 0.9 at a BPS conversion of 0.95, which occurred after 120 min. BPS disappearance in tetralin was described by the pseudo-first order rate constants indicated in Table 2. For reaction at 300°C, $k_{rel} = k_{TET}/k_{NEAT} = 0.087$, indicating that BPS reaction in tetralin was much slower than its disappearance during neat pyrolysis.

The effect of tetralin loading on the reaction of BPS was studied over the range $S_T = n_{TET0}/n_{BPS0}$ from 0.0 to 2.0 at 300°C. Increasing S_T simultaneously decreased BPS conversion (x) and increased selectivity ($s_i = y_i/x$) to the major products toluene and thiophenol. This is illustrated in Figure 3, where x and y_i/x are plotted vs. S_T for a constant reaction time of 50 min. During neat pyrolysis ($S_T = 0$) of BPS, x was approximately 0.9 after 50 min, whereas it was only 0.15 at $S_T = 2.0$ after the same reaction time. The selectivity to toluene increased from 0.4 to 1.0 and the selectivity to thiophenol increased from 0.1 to 0.8 as S_T increased from 0.0 to 2.0.

Reaction in Benzene. Reaction of BPS in benzene at 275°C at varying initial BPS concentrations allowed determination of an apparent overall reaction order. The resulting pseudo-first order rate constants for the disappearance of BPS are plotted vs. initial BPS concentration in Figure 4. The best-fit straight line has a slope of approximately 0.2, indicating an overall reaction order of 1.2 in BPS concentration over the range of conditions examined. The pseudo-first order rate constant corresponding to the neat pyrolysis concentration of 0.6 mol/L in Figure 4 is $4.47 \times 10^{-3} \text{ min}^{-1}$, somewhat less than the experimentally determined neat pseudo-first order rate constant of 0.01 min^{-1} at the same concentration.

Reaction with Thiophenol. Pyrolysis of BPS at 300°C in the presence of thiophenol with initial molar ratios [$S_{THP} = n_{THP0}/n_{BPS0}$] ranging from 0.0 (neat pyrolysis) to 1.68 yielded toluene, DPDS, and DPS as major products; diphenylmethane and bibenzyl were minor products. Figure 5 summarizes the temporal variation of product yields for $S_{THP} = 1.68$. The disappearance of BPS in the presence of thiophenol was characterized by a pseudo-first order rate constant of 0.0445 min^{-1} , comparable to that observed from neat pyrolysis.

The effect of added thiophenol on BPS decomposition is illustrated in Figure 6, a plot of BPS conversion and major product selectivities vs. S_{THP} for a constant reaction time of 20 min at 300°C. As S_{THP} increased from 0 to 1.68, x decreased from approximately 0.85 to 0.7, whereas toluene and DPDS selectivity (y_{TOL}/x_{BPS} ; y_{DPDS}/x_{BPS}) increased from 0.3 to 0.7 and 0.6 to 1.3, respectively. Evidently thiophenol functioned as a hydrogen donor to the benzyl radical, and the thus-formed phenylthiyl radical underwent termination by coupling.

Neat pyrolysis of Diphenyldisulfide. Neat pyrolysis of DPDS at 300°C yielded DPS as a primary product; thiophenol was a minor product. OPI was 0.9 at 60 min, which corresponded to a DPDS conversion and DPS yield of 0.7. Thus the selectivity of the reaction of DPDS to DPS was essentially 1.0, which implies the formation of elemental sulfur. The disappearance of DPDS was characterized by a pseudo-first order rate constant of 0.0196 min^{-1} .

DISCUSSION

The literature and present results for neat pyrolysis and reaction in tetralin combine to provide the basis for development of the mathematical model.

BPS Thermolysis Mechanism. The decomposition of BPS is reasonably interpreted as a set of free radical steps like those described by Attar (1978), Miller and Stein (1979), and Huang and Stock (1982). Illustrated in Figure 7a, a consistent sequence of steps is initiated through fission at the relatively weak (bond dissociation energy = 53 kcal/mol (Fixari et al., 1984)) C-S bond. BPS consumption also occurs through hydrogen abstraction by the initiation-generated benzyl or phenylthiyl radicals, which leads to toluene or thiophenol and a BPS radical. Abstraction of hydrogen from thiophenol by a benzyl radical will produce toluene and a phenylthiyl radical. Termination by radical recombination can involve: two phenylthiyl radicals, yielding DPDS; two benzyl radicals, producing bibenzyl; or other radicals (BPS radicals, for example), yielding unobservable, higher-molecular-weight oligomers. An additional elementary step is required to account for the minor amounts of diphenylmethane observed and also the secondary conversion of DPDS to DPS. Note that the latter might not actually occur in a single elementary step.

Pseudo-steady state analysis of the elementary steps of Figure 7 allows derivation of an analytical rate expression. Under the condition of a steady state, the rate of initiation must equal the rate of termination of radicals; we also consider the concentration of each radical β_1 , β_2 , and μ to be in a pseudo-steady state. Thus, with the overall BPS reaction rate as in Eq. 1,

$$r = [\text{BPS}](k_1 + k_2\beta_1 + k_3\beta_2) \quad (1)$$

the balances on β_1 and β_2 , which yield Eq. 2 and 3 for β_1 and β_2 , respectively,

$$\beta_1 = k_1[\text{BPS}]/(k_2[\text{BPS}] + k_5[\text{THP}]) \quad (2)$$

$$\beta_2 = \frac{1}{2} \left[-\frac{k_3[\text{BPS}]}{2k_4} + \sqrt{\left(\frac{k_3[\text{BPS}]}{2k_4}\right)^2 + \frac{2}{k_4}(k_5\beta_1[\text{THP}] + k_1[\text{BPS}])} \right] \quad (3)$$

allow formulation of the overall rate of decomposition as in Eq. 4.

$$r = k_1[\text{BPS}] \left\{ 1 + \frac{k_2[\text{BPS}]}{k_2[\text{BPS}] + k_5[\text{THP}]} + \frac{k_3^2[\text{BPS}]}{4k_1k_4} \left[\sqrt{1 + \frac{8k_1k_4}{k_5^2[\text{BPS}]} \left(\frac{k_5[\text{THP}]}{k_2[\text{BPS}] + k_5[\text{THP}]} + 1 \right)} - 1 \right] \right\} \quad (4)$$

For very low loadings of thiophenol, or at low conversion during neat pyrolysis, the rate expression of Eq. 4 reduces to

$$r = 2k_1[BPS] - \frac{(k_3[BPS])^2}{4k_4} \left(\sqrt{1 - \frac{8k_1k_4}{k_3^2[BPS]}} - 1 \right) \quad (5)$$

Thus the overall BPS reaction rate is a combination of a first-order term and higher-order terms and is therefore consistent with the experimentally determined reaction order of 1.2.

The dependence of r (Eq. 4) on the addition of thiophenol to the reaction mixture provides further scrutiny of the mechanism of Figure 7. This is the derivative of the rate with respect to thiophenol concentration, shown as Eq. 6.

$$\frac{dr}{d[\text{THP}]} = -\frac{k_1 k_2 k_5 [\text{BPS}]^2}{(k_2 [\text{BPS}] + k_5 [\text{THP}])^2} \left\{ 1 - \frac{1}{\sqrt{1 + \frac{8k_1k_4}{k_3^2 [\text{BPS}]} \left(1 + \frac{k_5 [\text{THP}]}{k_2 [\text{BPS}] + k_5 [\text{THP}]} \right)}} \right\} \quad (6)$$

Since the square root term in Eq. 6 is greater than unity, the term in the braces must be positive. Thus the rate of reaction decreases with increases in thiophenol loading. This is consistent with the observed decrease in conversion with the increase in thiophenol loading illustrated in Figure 6.

The observed effect of thiophenol loading on product selectivities also probes the candidate mechanism. According to Figure 7, the rate of toluene formation is

$$d[\text{TOL}]/dt = k_2\beta_1[\text{BPS}] + k_5\beta_1[\text{THP}] \quad (7)$$

which, after substitution for β_1 from Eq. 2 reduces to

$$d[\text{TOL}]/dt = k_1[\text{BPS}] \quad (8)$$

It is convenient to use the instantaneous selectivity $s_1 = dy_{\text{TOL}}/dx$ as a vehicle with which to analyze the overall selectivity $s_2 = y_{\text{TOL}}/x$. Since $r = [\text{BPS}]_0 dx/dt$ and $d[\text{TOL}]/dt = [\text{BPS}]_0 dy_{\text{TOL}}/dt$, s_1 is given as Eq. 9.

$$s_1 = d[\text{TOL}]/r = k_1[\text{BPS}]/r \quad (9)$$

Differentiation with respect to thiophenol concentration, holding [BPS] constant as in the present experiments, provides Eq. 10 as the sensitivity of the instantaneous selectivity to the addition of thiophenol.

$$ds_1/d[\text{THP}] = -k_1[\text{BPS}]r^{-2}(dr/d[\text{THP}]) \quad (10)$$

Thus, since $dr/d[\text{THP}]$ is always negative, as shown in Eq. 6, s_1 will always increase with increases in [THP]. Hence the increase in s_2 observed experimentally is consistent with the mechanism of Figure 7.

Likewise, the elementary step leading to DPDS suggests Eq. 11 for its formation rate.

$$d[\text{DPDS}]/dt = k_4 \beta_2^2 \quad (11)$$

This combines with the pseudo-steady state concentration of β_2 from Eq. 3 to allow formulation of Eq. 12

$$\frac{d[\text{DPDS}]}{dt} = \frac{k_4}{2} \left[-\frac{k_3 [\text{BPS}]}{2k_4} + \sqrt{\left(\frac{k_3 [\text{BPS}]}{2k_4}\right)^2 + \frac{2k_1 [\text{BPS}]}{k_4} \left(\frac{k_5 [\text{THP}]}{k_2 [\text{BPS}] + k_5 [\text{THP}] + 1}\right)} \right] \quad (12)$$

for the overall rate of formation DPDS. This, in turn, allows the determination of s_1 for DPDS and, hence, $ds_1/d[\text{THP}]$ for DPDS as Eq. 13.

$$\frac{d\left(\frac{d[\text{DPDS}]}{dt}\right)}{d[\text{THP}]} = + \frac{k_1 k_2 k_5 [\text{BPS}]^2}{(k_2 [\text{BPS}] + k_5 [\text{THP}])^2} \left\{ 1 - \frac{1}{\sqrt{1 + \frac{8k_1 k_4}{k_3^2 [\text{BPS}]} \left(1 + \frac{k_5 [\text{THP}]}{k_2 [\text{BPS}] + k_5 [\text{THP}]} \right)}} \right\} \quad (13)$$

Eq. 13 predicts that the selectivity to DPDS will increase as the concentration of thiophenol in the reaction mixture increases. This was observed experimentally, as shown in the plot of s_2 for DPDS vs. thiophenol loading of Figure 6.

Thermolysis of BPS in tetralin is by the neat pyrolysis steps and additional steps involving tetralin and its derived radicals. These are illustrated in Figure 7b, steady-state analysis of which allows formulation of the overall BPS reaction rate as Eq. 14:

$$r = k_1 [\text{BPS}] \left\{ 1 + \frac{k_2 [\text{BPS}]}{k_2 [\text{BPS}] + k_5 [\text{THP}] + k_6 [\text{TET}]} \right\} + \frac{k_3 (k_5 [\text{BPS}] + k_7 [\text{TET}])}{4 k_1 k_4} \left\{ \sqrt{1 + \frac{8k_1 k_4 [\text{BPS}]}{(k_2 [\text{BPS}] + k_7 [\text{TET}])^2} \left(\frac{k_5 [\text{THP}]}{k_2 [\text{BPS}] + k_5 [\text{THP}] + k_6 [\text{TET}]} + 1\right)} - 1 \right\} \quad (14)$$

In the limit of high tetralin loading, Eq. 14 reduces to $r = k_1 [\text{BPS}]$, less than one-half the rate predicted for neat pyrolysis. This is consistent with the experimentally determined rate constants listed in Table 2. Under these conditions, the rates of toluene and thiophenol formation are given by Eq. 15,

$$d[\text{TOL}]/dt = d[\text{THP}]/dt = k_1 [\text{BPS}] \quad (15)$$

which shows that added tetralin will increase the selectivity to both toluene and thiophenol.

CONCLUSIONS

1. Neat pyrolysis of benzylphenylsulfide was through a free-radical mechanism to toluene, thiophenol, and diphenyldisulfide. Pseudo-steady state analysis of consistent elementary steps allowed formulation of the rate expression as:

$$r = k_1 [\text{BPS}] \left\{ 1 + \frac{k_2 [\text{BPS}]}{k_2 [\text{BPS}] + k_5 [\text{THP}]} + \frac{k_3^2 [\text{BPS}]}{4 k_1 k_4} \left(\sqrt{1 + \frac{8 k_1 k_4}{k_3^2 [\text{BPS}]} \left(\frac{k_5 [\text{THP}]}{k_2 [\text{BPS}] + k_5 [\text{THP}]} + 1 \right)} - 1 \right) \right\} \quad (4)$$

Results of experiments with a set of co-reactants were consistent with the rate expression and aided in the elucidation of the mechanism.

2. The overall reaction order for pyrolytic decomposition of BPS was 1.2. This is consistent with the theoretical rate expression derived from the postulated mechanism.

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NOMENCLATURE

k_i	rate constant
n_i	mole number of i
OPI	Observed Product Index, $\sum \text{weight}_i / \text{weight}_{\text{BPS}_0}$
r	reaction rate, $\text{mol L}^{-1} \text{min}^{-1}$
S_i	coreactant loading, $n_{i_0} / n_{\text{BPS}_0}$
s_1	instantaneous selectivity of i , dy_i / dx
s_2	integral selectivity of i , y_i / x
x	conversion, $1 - n_{\text{BPS}} / n_{\text{BPS}_0}$
y_i	molar yield of i , n_i / n_{BPS_0}
$[]$	concentration, mol L^{-1}

Chemical Species

BPS	Benzylphenylsulfide, PhCH_2SPh
DPDS	Diphenyldisulfide, PhSSPh
DPS	Diphenylsulfide, PhSPh
THP	Thiophenol, PhSH
TOL	Toluene, PhCH_3

Greek Symbols

β_1	benzyl radical
β_2	phenylthiyl radical
μ	BPS radical

Subscripts

o	initial condition
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Table 1: Experimental conditions for the reactions of Benzyl Phenyl Sulfide.

Additive	Temperature (°C)	Major Products
Neat	275-386	Toluene, Thiophenol Diphenyldisulfide, Diphenylsulfide
Tetralin	300-386	Toluene, Thiophenol
Benzene	275	Toluene, Thiophenol Diphenyldisulfide, Diphenylsulfide
Thiophenol	300	Toluene, Diphenyl- disulfide, Diphenyl- sulfide

Table 2: Pseudo-first-order rate constants summarizing the reactions of Benzyl Phenyl Sulfide.

Temperature (°C)	Neat Pyrolysis	In Tetralin
275	0.0182±0.0039	-
300	0.0334±0.0019	0.0029±0.0006
340	0.175±0.045	0.0269±0.0008
386	0.530±0.046	0.3467±0.0284
$\log_{10}A(\text{min}^{-1})$	7.25	13.4
$E^*(\text{kcal/mol})$	22.6	41.7

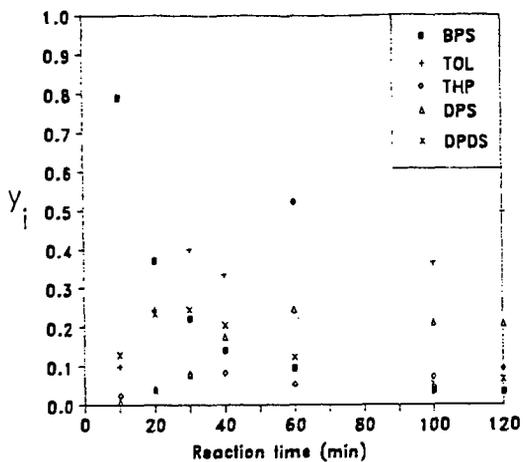


Figure 1: Temporal variation of the yields of the products of neat BPS pyrolysis at 300°C.

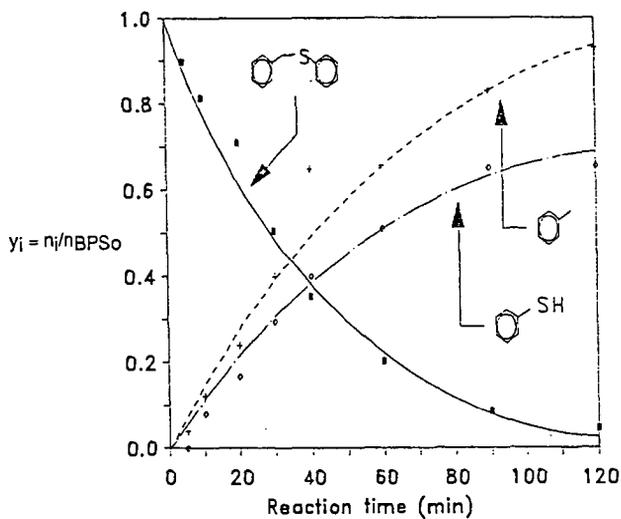


Figure 2: Temporal variation of the yields of the products of BPS thermolysis in tetralin at 340°C.

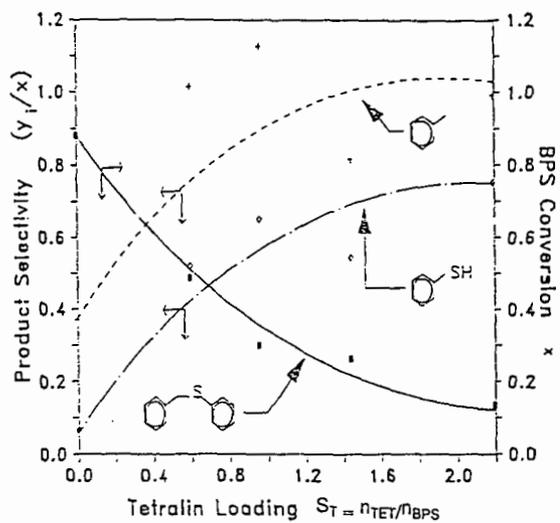


Figure 3: Dependence of product selectivity and BPS conversion on tetralin concentration during reaction at 300°C.

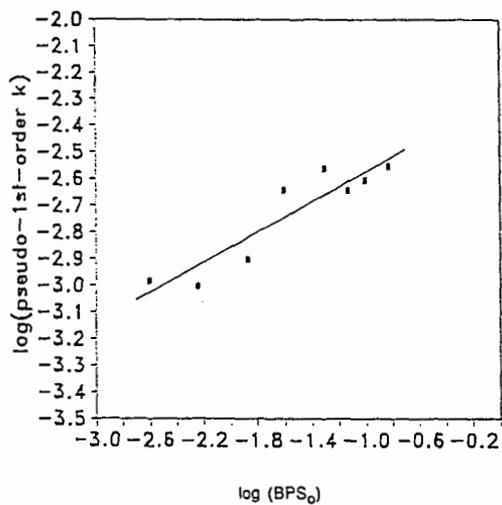


Figure 4: Overall order of reaction of BPS in benzene.

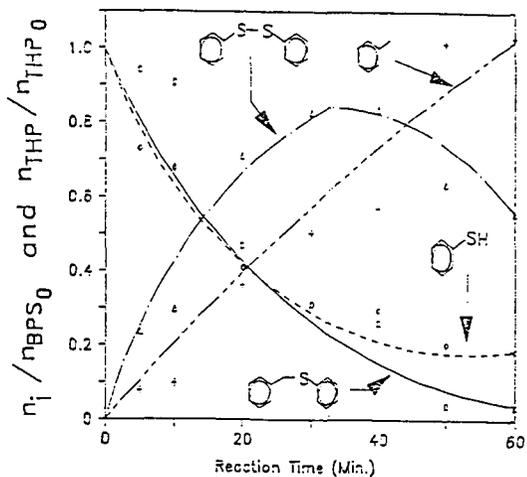


Figure 5: BPS pyrolysis at 300°C with added thiophenol: $S_{THP} = n_{THP}/n_{BPS} = 1.68$.

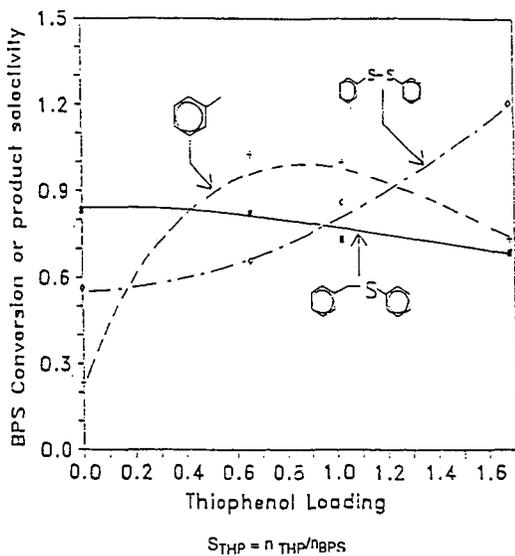


Figure 6: Dependence of product selectivity and BPS conversion on thiophenol concentration during reaction at 300°C.

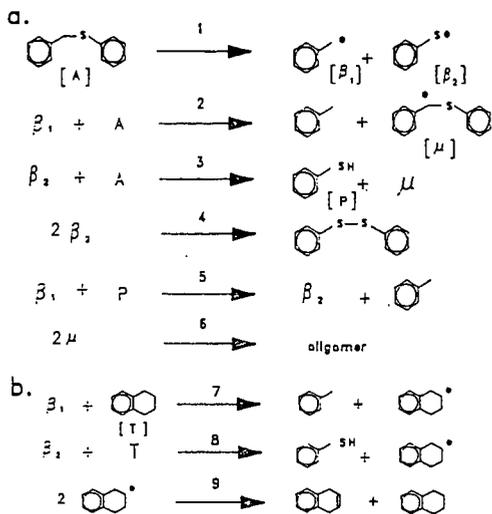


Figure 7: Free-radical steps for EPS reaction: (a) Neat pyrolysis; (b) Additional steps for reaction with tetralin.