

# Desulfuration of Aromatic Sulfones with Fluorides in Supercritical Water

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## Introduction

The existence of organic sulfur compounds (thiols, sulfides, and disulfides) in coals and heavy oils is well-known.<sup>1</sup> The removal of sulfur from these compounds is essential to avoid pollution. Presently, the sulfur removal is achieved by catalytic<sup>2</sup> or ionic<sup>3</sup> hydrogenation, photochemical oxidation,<sup>4</sup> or supercritical water (scw).<sup>5–8</sup> Since sulfones are easily obtained from organic sulfides by classical oxidation methods,<sup>9</sup> a known decomposition reaction of them,<sup>10–12</sup> named “sulfonyl extrusion”, is employed in our work. Although the mechanism of this reaction is presumably ionic, a radical mechanism also could be important. The first step of the base-induced reaction is probably to remove  $\beta$ -H from aromatic carbon, generating a carbanion;<sup>12</sup> the second step is the SO<sub>2</sub> elimination, which results in alkenes or alkynes from cyclic sulfones. Pyrolysis of sulfones at high temperatures (>300 °C) also yields alkenes/alkynes.<sup>10</sup> On the other hand, these reactive unsaturated compounds are probably intermediates in scw only, and the further reaction of them could be an addition of water or polymerization of monomers.

Fluoride ion is a very efficient and strong base in organic chemistry, if employing it in dry aprotic solvent.<sup>13</sup>

Table 1. Properties of Water at High Temperatures

property	25 °C	300 °C <sup>b</sup>
density [g/cm <sup>3</sup> ]	0.997	0.713
$\epsilon$	78.85	19.66
$\delta$ [MPa <sup>1/2</sup> ] <sup>a</sup>	47.9	29.7
$pK_w$	13.99	11.30

<sup>a</sup>  $\delta$  represents Hildebrand solubility parameter, and  $\delta^2$  is the cohesive pressure or energy density. It is proportional to the strength of H-bonding. <sup>b</sup> At its equilibrium pressure, approximately 8.2 MPa.

However, hydrogen bonds of protic solvents usually mask the fluoride ion by a specific solvation, and this makes fluoride ion a weak base. Interestingly, water at higher temperatures (>250 °C) behaves like an organic aprotic solvent. Density, dielectric constant, Hildebrand solubility parameter, and hydrogen bonding structure significantly decrease.<sup>14</sup> Therefore, water at high temperatures becomes more compatible for organic reactions (Table 1).

## Experimental Section

A 0.5 mmol quantity of sulfone (or phenyl sulfoxide) and 1.5 mmol of base were mixed with 6.0 mL of water in a pressure-resistant cell (int. vol. 10 mL) made of Hastalloy. Water and the cell were deoxygenated with argon, and the cell was connected with a temperature controller/heater (with two measuring and five heating rods), and pressure gauge. The average heating rate in the full temperature range was 21 °C/min. Interior temperature of cell was kept constant at 380 ± 1 °C, and pressure was 30 ± 2 MPa, respectively. The reaction time, which means a holding time at 380 °C, was 1 h. After cooling to room temperature for 1 h, the content of the cell was transferred into a 25 mL volumetric flask and then the cell interior was rinsed with acetone (in the case of KOH, dioxane was used). These washings were added to the cell content and the flask was leveled with acetone. A dark grayish fine powder deposit (presumably high-carbon containing, unsaturated hydrocarbons) was observed on the wall of the cell in all cases, except for using pure water and KBr, respectively. The sulfur was found as sulfite in aqueous phase after the reaction was completed. For the quantitative GC measurement of phenols and residual sulfones, a given quantity of a properly selected internal standard (4-hydroxybiphenyl, phenyl sulfone, dibenzothiophene 1,1-dioxide, and 4-fluorophenol, respectively) was added to the sample in order to determine the response factors. The concentrations of sulfones and phenols were determined accurately by calibrating the peak area with acetone solutions containing known concentrations of these components. The estimated error of measurement was ±0.5 mol %.

The GC-MS measurement was carried out using Shimadzu GCMS-QP5050A instrument with Column DB-1 (0.25 mm i.d.

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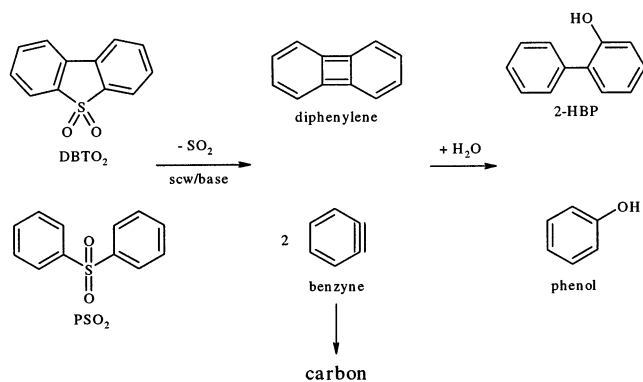
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**Scheme 1. On Desulfuration of Aromatic Sulfones with the Possible Intermediates**

× 28.5 m length, film 0.25 μm). GC temperature: 50–250 °C with heat-up rate of 10 °C/min; carrier gas: He at 100 kPa; flow rate: total 20 mL/min; split ratio: 8; column flow rate: 1.8 mL/min.

### Results and Discussion

In this work, desulfuration of two aromatic sulfones with fluorides in scw was studied, such as dibenzothioether 1,1-dioxide (DBTO<sub>2</sub>; a heteroaromatic sulfone) and phenyl sulfone (PSO<sub>2</sub>; the simplest aromatic sulfone), respectively. Acetone-soluble 2-hydroxybiphenyl (2-HBP) and insoluble dark, carbon-rich hydrocarbons are formed from DBTO<sub>2</sub>. Compared with the pure scw, the yield of 2-HBP is greatly increased using bases such as KOH and alkaline metal fluorides in scw. The reactivity of KF is higher than that of NaF, and the former is nearly as effective as KOH, which is known to be a much stronger base in aprotic solvents. Treatment of DBTO<sub>2</sub> with KF in subcritical water at 300 °C seems less effective (Table 2).

Fluoride ion is not only a proton base but also a nucleophile (i.e., carbon base) in dipolar aprotic solvents, since nucleophilic fluorination is well-known in organic synthesis.<sup>15</sup> The bromide ion in scw, which is a very weak proton base and strong nucleophile, is found less effective than pure scw itself. This result supports that fluoride ion probably does not attack the α-carbon bonded to a sulfur atom in a nucleophilic aromatic substitution reaction. Fluorine-substituted compounds are not detected in all these experiments.

Compared with DBTO<sub>2</sub>, desulfuration of phenyl sulfone (PSO<sub>2</sub>) with KF is not going with nearly quantitatively (>99.5%) yield under same conditions. Therefore, CsF is also employed because of its higher reactivity.<sup>13</sup> The reaction products are phenol, unreacted PSO<sub>2</sub>, and insoluble hydrocarbon. As can be expected, the yield of phenol increases using CsF in scw (Table 3). Therefore, the reactivity order of alkaline metal fluorides toward aromatic sulfones is concluded to be CsF > KF > NaF, which has the same order as that in aprotic solvents under normal conditions.<sup>13</sup>

In addition, reaction with KF in scw is also employed for phenyl sulfoxide (PSO), which is mainly deoxygenated to phenyl sulfide. However, a small amount of phenol is also formed. Moreover, our preliminary studies show that aliphatic sulfones (butyl and tetramethyl) are quantitatively (100%) decomposed with CsF in scw and results in the formation of a large amount of an insoluble dark-gray

**Table 2. Desulfurization of DBTO<sub>2</sub> in scw at 380 °C/1 h (in mol % of original DBTO<sub>2</sub>)**

base	2-HBP	DBTO <sub>2</sub>	base	2-HBP	DBTO <sub>2</sub>
H <sub>2</sub> O	8	92	KF	74	<0.5
KBr	4	96	KF <sup>a</sup>	35	41
KOH	79	<0.5	NaF	49	12

<sup>a</sup> In subcritical water at 300 °C.

**Table 3. Desulfurization of PSO<sub>2</sub> in scw at 380 °C/1 h (in mol % of original PSO<sub>2</sub>)**

fluoride	phenol <sup>a</sup>	PSO <sub>2</sub>
KF	50	40
CsF	65	23

<sup>a</sup> PSO<sub>2</sub> → 2 PhOH; the quantitative desulfuration would be equal with 200 mol % phenol.

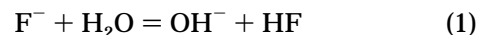
deposit and a small amount (1–2 mol %) of volatile hydrocarbons.

Fluoride ion was found to be a strong base in scw. It is probably able to deprotonate aromatic sulfones having weak C–H acidities (pK<sub>a</sub> > 30), and induces a sulfonyl extrusion reaction with high yield in scw. Our proposed mechanism of this reaction is based on the previous literature data<sup>10,12</sup> and is in agreement with structures of products that are formed in scw. Fluoride or hydroxide ion probably removes β-H from aromatic carbon, generating a carbanion, which can be stabilized by SO<sub>2</sub> elimination, resulting in diphenylene and benzyne, respectively. These highly reactive, unstable intermediates could be sources of insoluble hydrocarbons and phenols by water addition reactions, as well (see Scheme 1).

The reaction in the case of DBTO<sub>2</sub> gives higher yield in scw, compared with subcritical water. This could be explained by temperature (380 vs 300 °C) and solvent effects, which are due to the significantly different physical properties of scw. However, solubility of alkaline metal fluorides is supposed to be higher in subcritical water.

The basicity of fluoride ion in scw is comparable with that of the hydroxide ion. This might be attributable to much weaker solvation of fluoride (and hydroxide) ion in scw compared with liquid water at ambient temperature. Ions probably exist as ion pairs in scw, because of its low (ε < 20) dielectric constant.

However, the formation of hydroxide ion from water may also contribute in overall basicity:



In the case of very weak hydration, the shifting of equilibrium (1) to the right could be thermodynamically favorable. The reactivity of alkaline metal fluorides is found to be CsF > KF > NaF, which order is the same as that in aprotic solvents under ordinary conditions. The cation–fluoride ion interaction (increasing from CsF to NaF) and solubility of MF in scw (decreasing from CsF to NaF) could be responsible for this order.

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