

## A Study on the Photodegradative Behavior of the Dibenzothiophene (DBP) in Water System

Jae-Hyoun Kim

Department of Health Science, School of Natural Science Dongduk Women's University

### 수용액중의 디벤조치오펜의 광화학적 분해반응의 연구

김재현

동덕여자대학교, 자연과학대학, 보건관리학과

#### ABSTRACT

The present paper describes a study of the photochemical kinetics and its oxidation mechanism of DBT. The photolysis of DBT in aqueous solution media have shown to have significant oxidation activities for the photolytic desulfurization of DBT. The oxidation effect was more pronounced in 4 % NaCl solution. A mechanism was proposed that the desulfurization process arise from the substitution of sulfur by the hydroxyl radicals in different aqueous medium.

#### INTRODUCTION

The potential for ecological damage from oil spills have been reported for several decades. The residence time of oil could be so long that it seriously affect ecosystems in nearshore or offshore areas. In terms of air pollution, crude oil has been a notorious source of sulfur oxide compounds released from municipal sources and transportation.

Superoxide has been commonly found in petroleum distillates as well as in distillation residue.

Fuels, consisting of gasoline, petroleum naphtha, and kerosene, are among the distillates commonly ingested by aquatic biota (Bryson, 1986).

Some evidence indicates that oil products are toxic to algae, fish and marine invertebrates after exposure to air and light. Organic sulfur compounds have been used as markers of oil pollution to fish. Benzo[b]th-

iophene was bioconcentrated in fish to a greater extent than naphthalene and chrysene respectively (Orgata *et al.*, 1977).

Some toxicity experiments suggests that sulfur-analogs of PAH may be mutagenic or carcinogenic upon exposure to light (Wiest *et al.*, 1980).

Thiophene was documented to be more toxic, increasing its toxicity with the addition of benzene ring (Eastmond *et al.*, 1984). Derivatives of thiophenes were found to show mutagenic activity (Mcfall *et al.*, 1984).

Nonetheless, there has been lack of reports about the toxicity of dibenzothiophene.

Biological defulfurization of crude oil has been a potentially important process for dealing with marine oil spills in the ecosystem (Monticello and Finnerty, 1985).

Photolytic degradation process, however, was poorly studied in the light of the importance of ecologi-

cal risk assessment. Studies on the kinetics and transformation mechanism of photolytic oxidation of DBT selected for this study, are not only of theoretical importance, but also of significance to the sweetening process for desulfurization.

## EXPERIMENTAL

### 1. Procedure

Samples of DBT with initial concentration of 1 mg/L were prepared in 1% acetonitrile solution. The experiment was conducted using a blacklamps to simulate sunlight. A merry-go-round photoreactor with 10 20-watt photoreactor lamps with major output at 350 nm was used in the experiments. All test solutions received equal radiation from the radiation source with a distance from the test tubes to the lamp. After exposure a time intervals, samples were taken for analysis by GC to determine the remaining concentration of the parent compound. 1 mL of the test samples was withdrawn from the test tubes. 0.5 mL of hexanol was added to the sample, which was then shaken vigorously for about 1 min and kept in the cold room for GC analysis. The reaction tubes were tightly sealed with Teflon liner cap.

#### 1) Kinetic study

##### (1) $\text{H}_2\text{O}_2 + \text{Fe}^{++}$

In the total solution of 10 mM  $\text{H}_2\text{O}_2$  and 0.2 mM  $\text{Fe}^{++}(\text{FeSO}_4)$ , 1 mg/L DBT was added in test tubes from the the stock solution. The solution was pored into separate test tubes and photolysis was conducted at different time intervals. The control samples were then kept in the dark chamber during exposure.

##### (2) air bubbling

The solution in test tubes was bubbled to saturate oxygen for 1 min and then added a aliquot of DBT stock to make 1 mg/L DBT concentration in each test tube. Tubes were kept tightly before exposure to light source.

##### (3) sludge water and air bubbling

The primary effluent was filtered through a 0.45

$\mu\text{m}$  glass fiber filter (Whatman) to get rid of sludge for the experiment. Average cell count was about  $9 \times 10^8$  cells/mL. The filtered effluent was diluted 10 times with distilled water and added DBT in test tubes after saturation with air. 2 mL of sludge water was added into air-saturated solution, which was then mixed throughly and exposed under the sunlamp for 5 day.

##### (4) 4% NaCl in conjunction with air-bubbling

1 mL of 40% of NaCl solution (stock) was added into air-saturated samples prepared in different medium to make 4% saline water, and then exposed for the same period to compare the effect of salinity. Same experiment was conducted without NaCl at the same time for the control.

#### 2) Photoproduct Study

A photoreaction in substrate solution was carried out in a 2 L batch Pyrex flask. Same photolysis apparatus was used as for the kinetic experiment. After 6-day exposure, samples were extracted for determination of the DBT photoproducts which solutions were characterized by GC/MS.

## ANALYTICAL METHOD

The hexanol extract was evaporated for concentration to 2 mL under nitrogen flow. 1  $\mu\text{L}$  of the sample was injected into the GC for analysis with the following conditions: temperature: 80°C for 1 min, then 20 °C/min to 260°C, hold for 20 min; detector: FID at 300°C; injector temperature: 250°C; carrier gas: nitrogen at 1.5 ml/min. By comparing their peak areas with those of known standard peaks obtained from the direct injection, a recovery of 95% was achieved. All the methanol extracts were cleaned up prior to GC analysis while the hexanol extracts were injected directly into the GC. A surrogate standard used was naphthalene. Identification was performed by co-chromatography with known standards and quantification by comparing peak areas with those of known calibrated standard peak areas using an automatic integrator. The photoproduct identification was fur-

ther achieved by GC/MS with EI analysis, N<sub>2</sub> gas carrier at a flow rate of 1.5 mL/min at 70 eV and similar GC conditions.

**RESULTS AND DISCUSSION**

It is evident from our results that it is indeed possible to degrade substantial concentrations of DBT through the use of a mixture of oxidant. The oxidation of DBT appears to require the presence of air or H<sub>2</sub>O<sub>2</sub>. An enhancement in the rate was demonstrated for 4% NaCl solution in conjunction with air bubbling when compared to that of distilled water.

1) Kinetic study

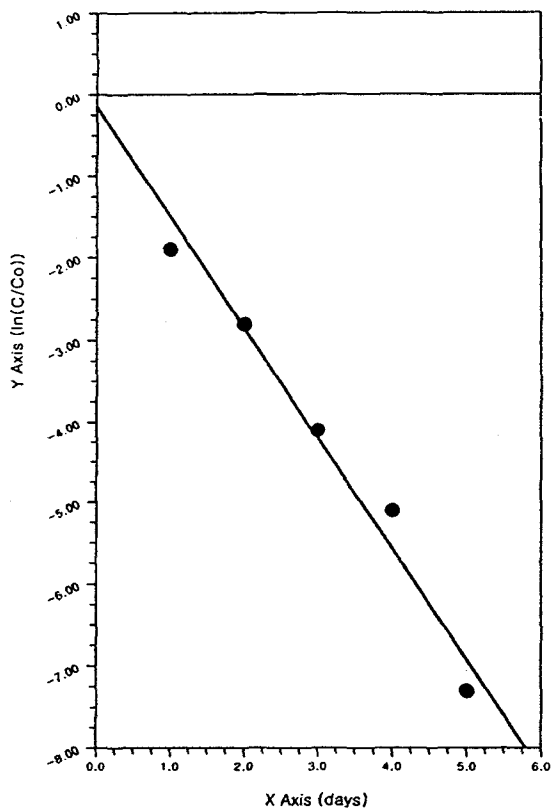
In the photo-oxidation of the DBT, the overall rates of reaction were followed by monitoring the decrease of the parent compound (Figs. 1, 2, 3 and 4).

Each point in each figure represents the data from an individual experiment. In order to determine the photolysis rate ( $k_d$ ) of DBT, the slope of  $\ln(C/C_0)$  vs time (days) using the least squares method was plotted. Plots of  $\ln(C/C_0)$  vs. time of DBT were generally linear generally greater than 0.96 except for air-bubbling system. The disappearance rates ( $k_d$ ) and half-lives (days) for each DBT are summarized in Table 1.

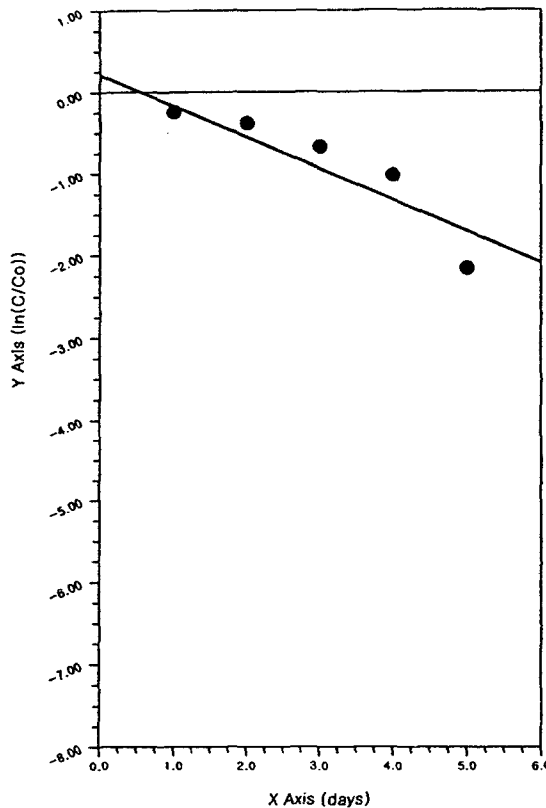
**Table 1.** Disappearance kinetic rates ( $k_d$ ) and half-lives (days) of DBT

| medium types                                          | $k_d$  | $t_{1/2}$ (days) | r    |
|-------------------------------------------------------|--------|------------------|------|
| 1. H <sub>2</sub> O <sub>2</sub> and Fe <sup>++</sup> | -1.357 | 0.51             | 0.98 |
| 2. Air bubbling                                       | -0.312 | 2.10             | 0.92 |
| 3. sludge water + air                                 | -1.089 | 1.04             | 0.96 |
| 4. 4% NaCl+air bubbling                               | -1.314 | 0.52             | 0.98 |

r: correlation coefficient



**Fig. 1.** Kinetic plot for the photolysis of exposed samples of DBT in H<sub>2</sub>O<sub>2</sub> and Fe<sup>++</sup> system.



**Fig. 2.** Kinetic plot for the photolysis of exposed samples of DBT with air bubbling.

Loss of the chemical by means other than photodegradation was measured by analysis of the dark control samples. The kinetic rates of the experiment was subtracted from the rates of photolyzed samples.

#### (1) $H_2O_2$ and $Fe^{++}$

Recently, hydroxyl radicals were widely regarded as one of chemical intermediates for the degradation of various aromatics. The OH. produced in aqueous phase were effective in the reaction of these compounds (Sedlak and Andern, 1990).

#### (2) Effect of air bubbling

Fig. 2 shows the photoreduction rate of the DBT in water phase by the air bubbling that facilitate the reaction. The r value was relatively lower than that of other systems.

#### (3) Effect of air bubbling in sludge water

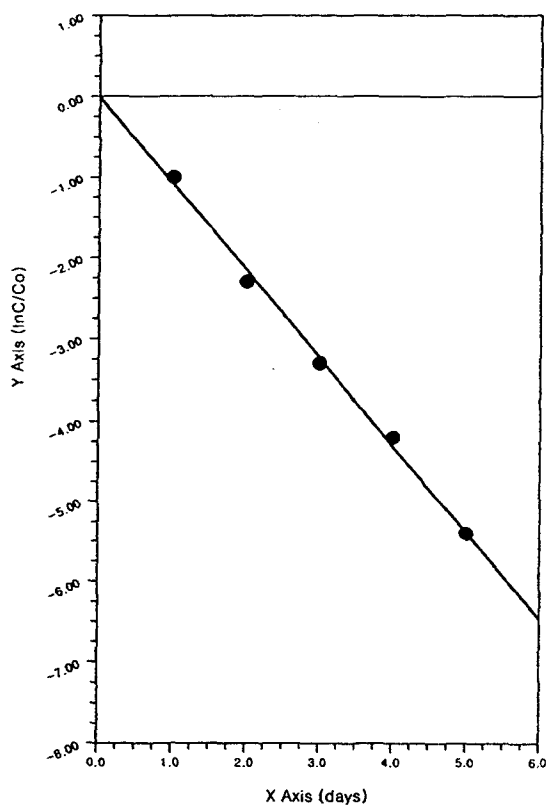


Fig. 3. Kinetic plot for the photolysis of exposed samples of DBT in air bubbling and sludge water system.

The decomposition rate of DBT in the media was doubled, compared to the experiment of air-bubbling only, as was shown in Fig. 3.

#### (4) Effect of NaCl

Salinity was a significant factor which shows an enhancement factor on photodegradation. The data indicates that 0.4% salinity in air-saturated solution almost increased photodegradation rate 4 times higher than the rate without salinity in same condition

Table 2. Identification of the compound by spectrum fragmentation

| m/e | relative intensity | preliminary remarks |
|-----|--------------------|---------------------|
| 216 | 100%               | $M^+$               |
| 188 | 19%                | $M^+ - CO$          |
| 187 | 60%                | $H^+$ abstraction   |
| 168 | 32%                | $SO$ abstraction    |
| 160 | 39%                | $CO$ abstraction    |

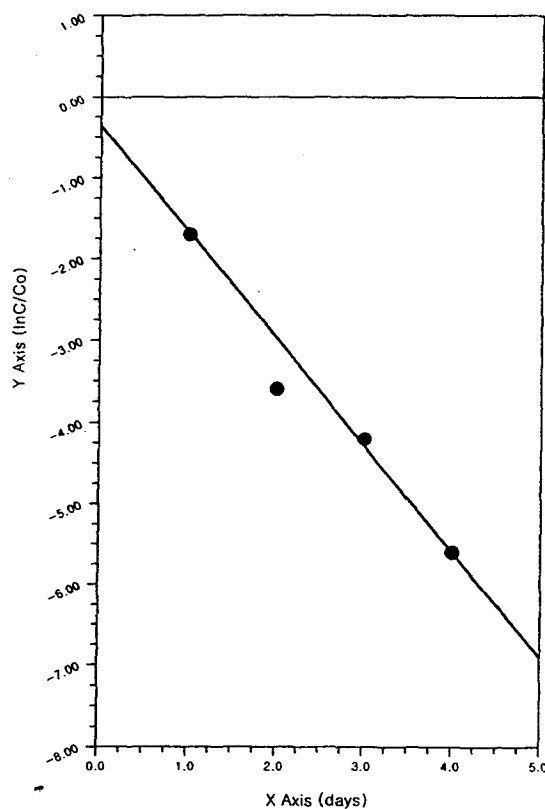


Fig. 4. Kinetic plot for the photolysis of exposed samples of DBT in NaCl solution.

(Table 1).

2) Photoproduct study

The photolysis reaction appears to be affected by

the three test medium. A general mechanism for the photooxidation of DBT is outlined in Scheme 1.

Oxidation reactions of DBT in water phase photopro-

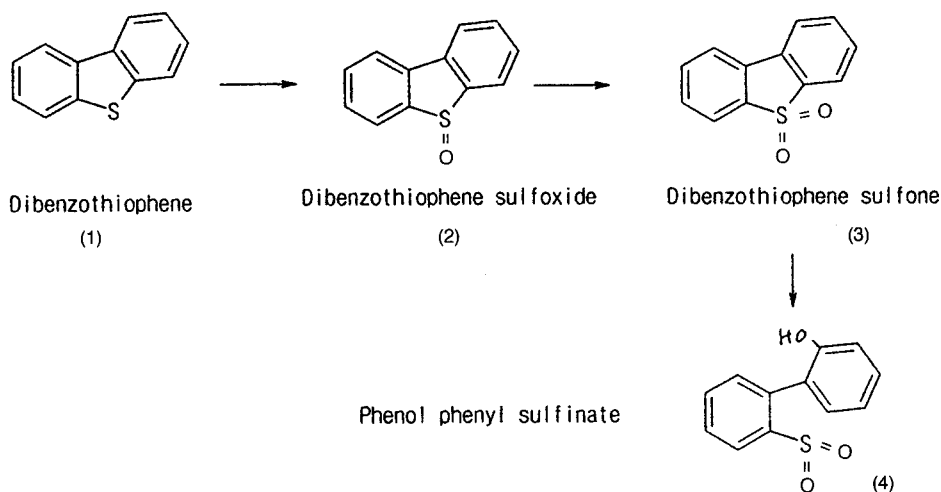


Fig. 5. Proposed pathway for photodegradation of DBT in aqueous system.

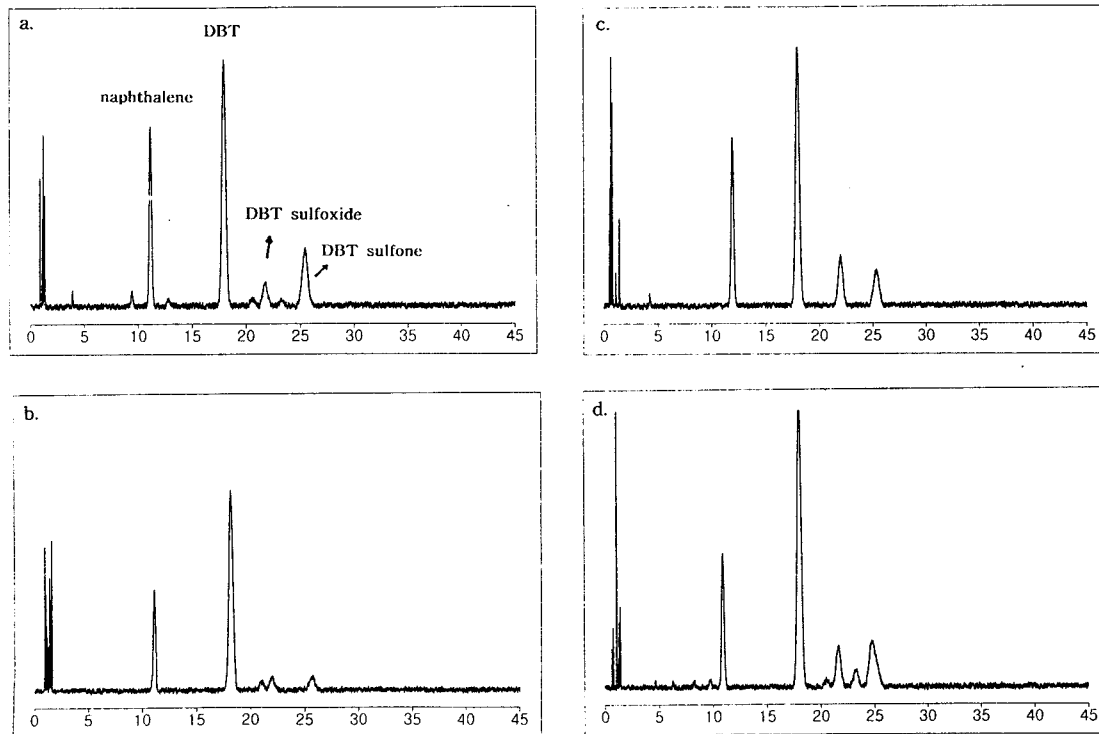


Fig. 6. The GC chromatograms of photoproducts in exposed and control samples. (a. 5-day exposed in  $Fe^{++}$  and  $H_2O_2$  system; b. 5-day exposed in air bubbling; c. 5-day exposed in air and sewage; d. 3-day exposure with NaCl.

duced dibenzofuran through the oxidation to dibenzothiophene sulfoxide and dibenzothiophene sulfone, as investigated before (Abdali, 1990). The formation and disappearance of secondary photoproducts were not observed during exposure time. It is assumed that phenol phenyl sulfinate may be produced as a subsequent mechanism (Fig. 5-(4)).

Dibenzothiophene sulfone was injected into the GC/MS to confirm its identity with the peak with fragmentation of 216, 188, 187, 168, 160 corresponding to  $M^+$  and loss of  $-CO$ ,  $-H^+$ ,  $-SO$  and  $-CO$  respectively. The relative intensity and  $m/e$  values are listed in Table 2.

### CONCLUSIONS

The photodegradation of DBT initiated by in different medium was studied where intermediate oxidation products were observed. The rates of photodegradation, as followed by DBT oxide and DBT sulfone formation, showed difference on the kinetic rates. Good linearity in plots was also observed, implying that such relationships may provide a good indication of the subsequent degradation processes.

Even though DBT in the mixture of oil/water system was not really photodegraded well (Abdali, 1992), it worth mentioning that the saltout effect of NaCl is very effective to solubilizes the DBT to photodegrade into water system.

### REFERENCES

- Abdali, F.K. (1990) Studies on the photolytic behavior of benzothiophene in crude oil/water systems. Thesis (Ph.D), Dept. Environ. Health. University of Michigan.
- Eastmond D.A., G.M. Booth and M.L. Lee (1984). Toxicity, accumulation, and elimination of polycyclic aromatic sulfur heterocycles in *Daphnia magna*. Arch. Environ. Contam. Toxicol. 13:105-111.
- Mcfall T, G.M. Booth, M.L. Lee, Y. Tominaga, R. Pratap, M. Tedjamulia and R.N. Castle (1984). Mutagenic activity of methyl-substituted tri- and tetracyclic aromatic sulfur heterocycles. Mutat. Res. 135: 97-103.
- Mill, T., W.R. Mabey, B.Y. Lan and A Baraze (1981) Photolysis of polycyclic aromatic hydrocarbons in water. Chemosphere, 10(11/12): 1281-1290.
- Monticello, D. J. and W.R. Finnerty (1985) Riding the fossil fuel biodesulfurization wave. Annu. Rev. Microbiol., 39:371-389.
- Orgata, M., Y. Miyake, S. Kira, K. Matsunaga and M. Imanaka (1977) Transfer to fish of petroleum paraffins and organic compounds. Water Res. 11:333-338.
- Sedlak, D.L. and Andren, A.W. (1991) Oxidation of chlorobenzene with Fenton's Reagent. Environ. Sci. Technol., 25(4): 777-782.
- Wiest F. De., R.G. Winkler, J. Gielen and D. Ronida (1980). Influence of near ultraviolet irradiation on the mutagenicity of polynuclear aromatic hydrocarbons adsorbed on carbon black. In: Polynuclear aromatic hydrocarbons chemical analysis and biological fate. Fifth International Symposium, Battelle Press, Columbus, Richland. pp. 33-41.