

# Photochemical degradation of carbon tetrachloride mediated by 3-R-2(3H)-benzothiazol-2-ones and ultrasound effect on this degradation

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## Abstract

The photodecomposition of carbon tetrachloride ( $\lambda_{\text{irr}} > 290 \text{ nm}$ ) was studied in the presence of 3-R-2(3H)-benzothiazol-2-ones, where R was benzyl-, methyl- or hydrogen as electron donors. Degradation of  $\text{CCl}_4$  is a function of structure electron donors. The reaction course was followed by measuring the HCl and  $\text{C}_2\text{Cl}_6$  evolutions. Very low concentrations of  $\text{C}_2\text{Cl}_6$  were detected both in sonicated and silent photochemical experiments. Ultrasound accelerates HCl formation, and the rate is a function of R in the mediator, being the highest for R = methyl and the lowest for R = hydrogen. An attempt at explanation is given for these observations.

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## 1. Introduction

In previous papers [1,2], we studied the photolysis of 2-sulfanylbenzothiazoles in methanol and heptane solutions. Similarly to other thioethers, the radical cleavage of the S–R bond was observed, and proved to be much easier in heptane than in methanol. Side reactions, occurring in experiments run in an air atmosphere, were oxidations producing sulfoxides and sulfones. Irradiation of halocarbons at an appropriate UV-wavelength causes their dehalogenation, especially in the presence of electron donors [3], such as amines [4], dienes [5], and sulfides [6] by interaction of the halogenated compounds with the excited state of the electron donor [7], or vice versa [8].

On the other hand, several papers show that carbonyl compounds, e.g. acetone, can act as sensitizers for  $\text{CCl}_4$  photolysis [9–11], with HCl as a final product [12,13], and in the presence of oxygen, phosgene as one of the main products [13]. Gas phase photolysis of the mixture of  $\text{CCl}_4$  and pentan-3-one generates small amount of  $\text{C}_2\text{Cl}_6$  [14].

The main purpose of this work was thus to check experimentally the effect of combining in the same molecule the structural elements, a benzothiazole ring and a carbonyl group, which displays sensitizer activities in the photolysis of  $\text{CCl}_4$  and to examine if their effect will be similar as described for 2-sulfanylbenzothiazoles [15].

## 2. Experimental details

### 2.1. Materials

3-Methyl-2(3H)-benzothiazol-2-one (MeBTO), 3-benzyl-2(3H)-benzothiazol-2-one (BnBTO) and 2(3H)-benzothiazolone-2-one (BTO), from SYNKOLA Co., were recrystallized from ethanol or acetonitrile. Carbon tetrachloride (Lichrosolv grade, Merck Co.) was used without further purification. Redistilled water was used throughout this study.

### 2.2. Analytical methods

UV–VIS spectra were measured at room temperature in  $\text{CCl}_4$  solution using a Diode Array Spectrophotometer HP

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8452 A. HRGC analyses were performed on a gas chromatograph (Hewlett-Packard 5890a Series II) equipped with split-splitless injector (300 °C, splitting ratio 1:30), a flame ionization detector operated at 300 °C, and a CP-SIL 5 CB (Chrompack) cross-linked fused-silica capillary column (10 m × 0.32 mm i.d.) coated with 0.25 μm-thick polydimethylsiloxane. The oven temperature was programmed from 40 to 320 °C at 20 °C min<sup>-1</sup>. Helium (Tatragas, 99.995%) was used as the carrier (inlet pressure 50 kPa). Air and hydrogen flow rates were 300 and 30 ml min<sup>-1</sup>, respectively. The injection volume was 0.5 μl, with *n*-tetradecane or *p*-cresol as internal standards. The chromatograms were processed with a HP Chemstation 3365-II. Mass spectra (electron impact 70 eV) and reconstructed total ion chromatograms were obtained by automatic scanning in the mass range *m/z* 30–35 at 2.2 scans s<sup>-1</sup>.

Isotachopheresis analyses of the samples were performed on an analyzer ZKI-02 (LABECO Co., Spišská Nová Ves, Slovakia) using a joint-column technique. The diameter of the pre-separation column was 0.8 mm, and 0.3 mm for the analytical column. Both columns were equipped with a conductivity detector. For chloride ion determination, the electrolyte system used was: solvent, H<sub>2</sub>O; leading anion, 10 mmol l<sup>-1</sup> nitrate; counter ion, Cd<sup>2+</sup> β-alanine; additive, 0.1% (w/v) methyl hydroxyethyl cellulose (MHEC), pH 3.7; terminating anion, 10 mmol l<sup>-1</sup> tartrate, pH 7. Cl<sub>2</sub> and HClO were reduced in every sample with potassium iodide prior to isotachopheresis analysis.

### 2.3. Experimental set up

All the experiments were carried out with the set up described previously [16], consisting in a photochemical reactor equipped with a glass (SIMAX) insertion cell and the ultrasound emitter (25 kHz, 16 W cm<sup>-2</sup>). Temperature was kept constant at 22 °C by circulation of water.

The UV light source was a mercury 125 W lamp from Tesla Holešovice, Czech Republic. Photolyses and sono-photolyses were performed with 100 ml of 2 × 10<sup>-2</sup> M solutions of the appropriate electron donor in CCl<sub>4</sub>. Wa-

ter (50 ml) was added to the reaction cell (upper layer), to trap the hydrogen chloride evolved. The samples were thoroughly de-aerated by continuous bubbling of nitrogen through the solution, before and during the irradiations. Progress of the reaction was monitored by withdrawal of aliquots from the water or CCl<sub>4</sub> layers, which were analyzed by isotachopheretic method (Cl<sup>-</sup> and carboxylic acids) or UV-VIS (donors). The time dependence of C<sub>2</sub>Cl<sub>6</sub> formation was examined discontinuously: for each reaction time, an experiment was performed with a fresh solution of the electron donor in carbon tetrachloride; immediately after the irradiation was stopped, the mixture was concentrated and analyzed for the content of C<sub>2</sub>Cl<sub>6</sub> in carbon tetrachloride and Cl<sup>-</sup> in water.

All the experiments, with and without sonication, were performed under identical conditions.

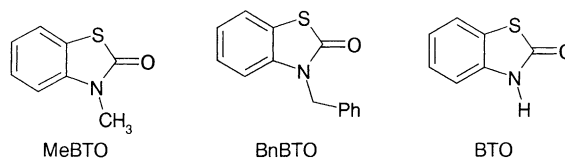
### 2.4. Theoretical computation

Geometry of studied molecules was optimized using AM1 method. Energies of molecular orbitals were computed using ab initio HF/6-31+G\*\* for ground states and CI/6-31+G\*\* for excited states.

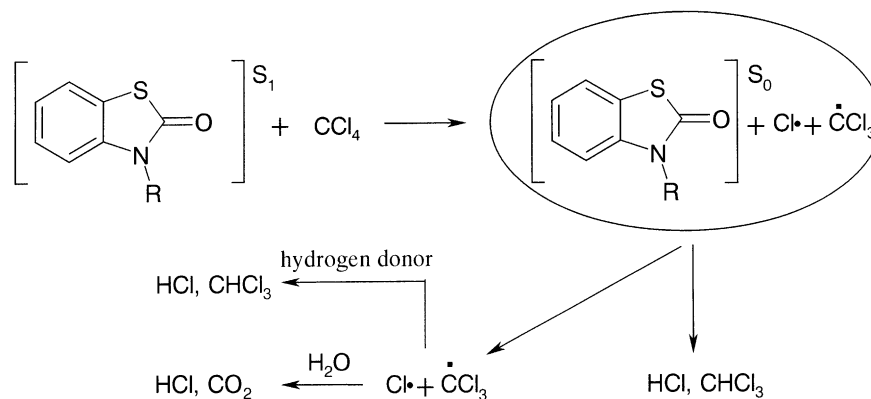
## 3. Results and discussion

The following benzothiazole derivatives were used in our study of carbon tetrachloride photolysis: MeBTO, BnBTO and BTO (Scheme 1).

By measuring the amounts of HCl and C<sub>2</sub>Cl<sub>6</sub> formed, it appears clearly that CCl<sub>4</sub> is decomposed under these



Scheme 1. The structure of benzothiazole sensitizers under study.



Scheme 2.

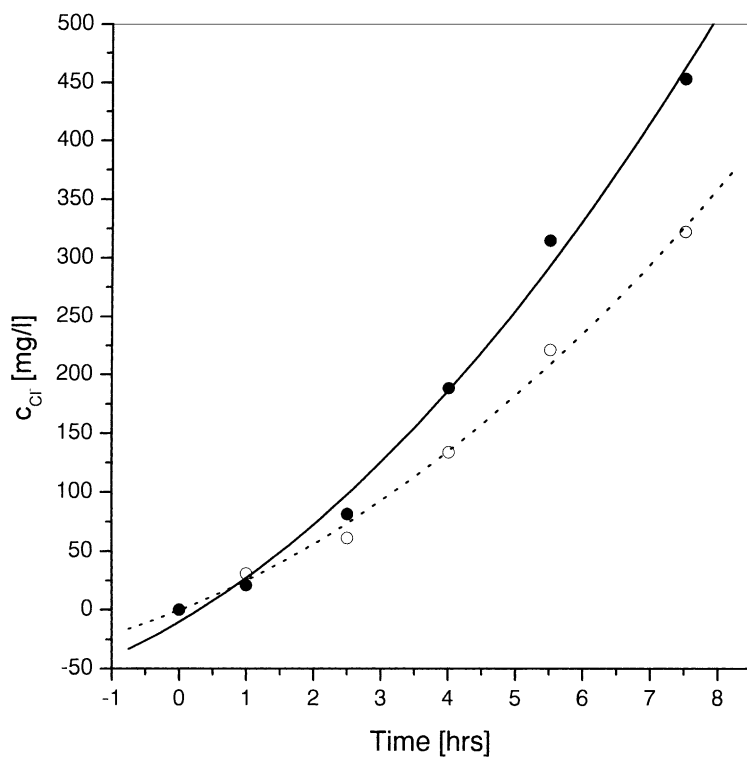


Fig. 1. Time course of  $\text{Cl}^-$  formation in the photolysis of MeBTO in  $\text{CCl}_4$  solution ( $c = 2 \times 10^{-2} \text{ mol dm}^{-3}$ ) with (●) and without (○) sonication.

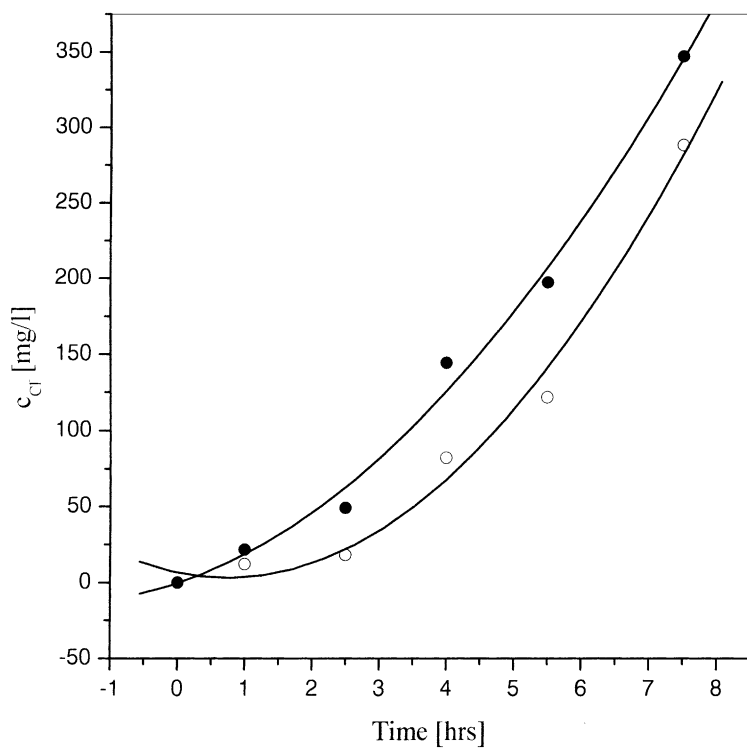


Fig. 2. Time course of  $\text{Cl}^-$  formation in the photolysis of BnBTO in  $\text{CCl}_4$  solution ( $c = 2 \times 10^{-2} \text{ mol dm}^{-3}$ ) with (●) and without (○) sonication.

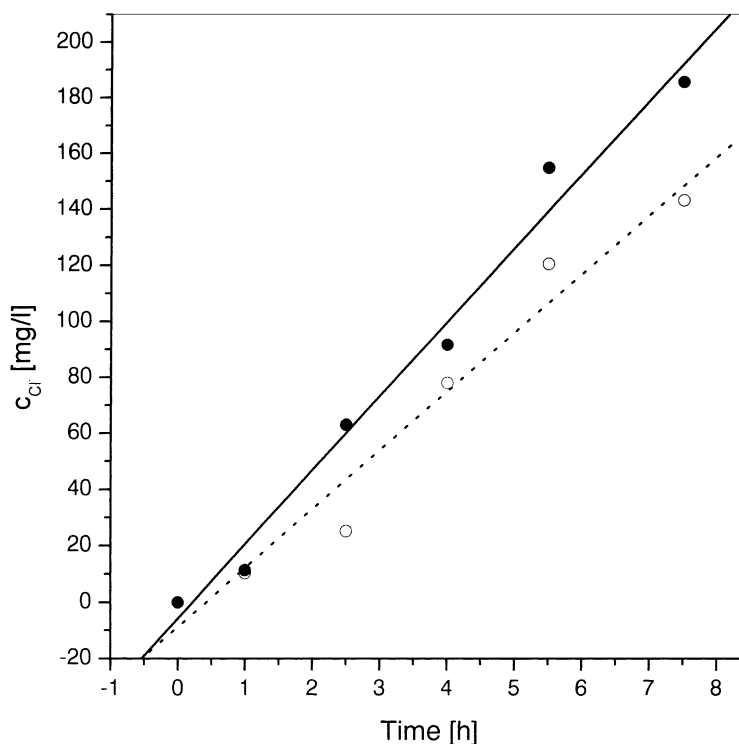


Fig. 3. Time course of  $\text{Cl}^-$  formation in the photolysis of BTO in  $\text{CCl}_4$  solution ( $c = 2 \times 10^{-2} \text{ mol dm}^{-3}$ ) with (●) and without (○) sonication.

conditions. However, in contrast with the previous work [15], only low and variable amounts of  $\text{C}_2\text{Cl}_6$  were observed with MeBTO and BnBTO as sensitizers, and  $\text{C}_2\text{Cl}_6$  was not detected when using BTO, even after concentration of the mother solution.

The first step of the sequence, the initial cleavage of the C–Cl bond, requires the presence of the sensitizer, making probable an energy transfer from the excited benzothiazole-2-one molecules to  $\text{CCl}_4$  (Scheme 2). The comparison of the results from sono-photo and silent photochemical experiments shown in Figs. 1–3 and Table 1 support the assumption that ultrasound facilitates the electron energy transfer from the excited state of the sensitizer to the  $\text{CCl}_4$  molecules. (The rate of HCl formation is much higher in sono-photo experiments.)

Table 1  
Results of photo- and photo-sono-degradation of  $\text{CCl}_4$

| $t$ (h) | $[\text{Cl}^-]$ ( $\text{mg dm}^{-3}$ ) |                 |                    |       |       |       |
|---------|---|-----------------|--------------------|-------|-------|-------|
|         | MeBTO <sup>a</sup>                      | US <sup>b</sup> | BnBTO <sup>a</sup> |       | BTO   |       |
| 0       | 0                                       | 0               | 0                  | 0     | 0     | 0     |
| 1       | 21.0                                    | 31.1            | 12.0               | 21.65 | 10.3  | 11.4  |
| 2.5     | 61.3                                    | 81.3            | 18.1               | 48.9  | 25.1  | 63    |
| 4       | 133.7                                   | 188.1           | 82.1               | 144.3 | 78.0  | 91.6  |
| 5.5     | 221.1                                   | 314.3           | 121.5              | 196.8 | 120.4 | 154.7 |
| 7.5     | 321.8                                   | 452.6           | 287.9              | 346.6 | 142.9 | 185.5 |

<sup>a</sup> Photochemical experiment.

<sup>b</sup> Photo-sonochemical experiment.

Table 2  
Amount of non-ionogenic chloro compounds after 7.5 h photolysis

|     | MeBTO <sup>a</sup> | US <sup>b</sup> | BnBTO <sup>a</sup> | BTO  |      |
|-----|--------------------|-----------------|--------------------|------|------|
| %Cl | 0.71               | 1.22            | 0.70               | 1.32 | 2.26 |

<sup>a</sup> Photochemical experiment.

<sup>b</sup> Photo-sonochemical experiment.

According to this view, both Cl and  $\text{CCl}_3$  radicals react further with hydrogen donors, chlorine atoms giving HCl, and  $\bullet\text{CCl}_3$  giving  $\text{CHCl}_3$ , which was detected on GC–MS in preference to dimerization. Radical chlorination of the BTO compounds was shown to be a minor pathway. The results given in Table 2 show that this reaction is of little importance under silent conditions. Even if it increases by ca. 20–60% in sono-photochemical experiments, it remains much smaller than in 2-sulfanylbenzothiazole-sensitized reactions [15].

The proposed mechanism, which contrasts with the exciplex route followed in the presence of 2-sulfanylbenzothiazoles [15], is supported by the work of Pavlik et al. [17]

Table 3  
Energy of HOMO and LUMO orbitals in ground and singlet excited states

|                    | MeBTO (eV) | BnBTO (eV) | BTO (eV) |
|--------------------|------------|------------|----------|
| HOMO <sub>S0</sub> | −8.47      | −8.39      | −8.51    |
| LUMO <sub>S0</sub> | 1.62       | 1.57       | 1.46     |
| HOMO <sub>S1</sub> | −8.47      | −8.39      | −8.51    |
| LUMO <sub>S1</sub> | 1.62       | 1.57       | 1.46     |



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