

Effect of ultrasound on the photolysis of carbon tetrachloride mediated by benzothiazole derivatives. 2-Sulfanylbenzothiazoles

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The photodecomposition of carbon tetrachloride was studied under sonication in the presence of *N*-(*tert*-butyl)-benzothiazole-2-sulfenamide (TBBS), *N*-(cyclohexyl)benzothiazole-2-sulfenamide (CBS), and 2-sulfanylbenzothiazole (MBT) as electron donors. By following the concentrations of Cl⁻ and C₂Cl₆ as a function of time, it was shown that ultrasound decreases their rate of formation when TBBS and CBS were used, but it has no effect in the presence of MBT. These observations were rationalized by a cavitation-induced destabilization of the contact ion pair (CIP) formed from exciplexes.

Introduction

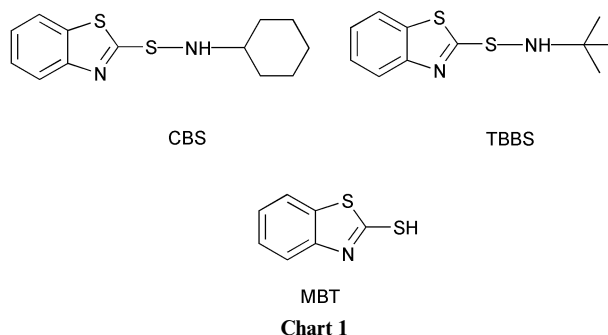
Irradiation of halocarbons at an appropriate UV-wavelength causes their dehalogenation, especially in the presence of electron donors,¹ such as amines,² dienes,³ and sulfides.⁴ This bimolecular reaction proceeds *via* excimers,^{5,6} formed by interaction of the halogenated compounds with the excited state of the electron donor,^{7,8} or *vice versa*.⁹

Sonochemistry has become one of the well recognized new techniques in chemistry,¹⁰ with numerous applications, especially useful for heterogeneous¹¹ and electrochemical¹² reactions. The beneficial effects of ultrasound are attributed to improved mass transfer and surface cleaning (at the electrode in electrochemical systems). In homogeneous reactions it is less easy to determine the origin of the effects.¹³ Nevertheless, several recent papers have described the role of ultrasound in the homogeneous phase degradation of halocarbons.¹⁴

Some years ago,¹⁵ we started a study of the effects of ultrasound on a few important photochemical reactions, such as additions, isomerizations and olefin dimerizations. We found that acoustic waves have no effect on unimolecular reactions, but accelerate bimolecular ones,^{15,16} probably because of a more even distribution of the reactive excited states throughout the solution by the cavitation-induced "ideal agitation".¹⁷ Furthermore, in bimolecular reactions such as cycloadditions, where regio- or stereo-isomeric products can form, sonication was shown to affect their ratio significantly. The quenching of triplet states or the disruption of intermediate excimers or exciplexes can be responsible for these alterations, a conclusion also reached from our study of the sono-photochemical pinacolization of benzophenone.¹⁸

The positive effect of ultrasound, *i.e.* rate enhancement, was observed in the TiO₂-mediated photolysis of 2,4,6-trichlorophenol,¹⁹ and Compton *et al.*²⁰ found that using a TiO₂ semiconductor electrode as an ultrasonic emitter also increases the efficiency of the photo-electrolyses of water or 2,4-dichlorophenol in acetonitrile. The TiO₂-catalyzed decomposition of trifluoromethyl phenyl ketone occurs faster (1.4 to 1.9 times) under simultaneous sonication and UV irradiation in aqueous solution,²¹ with an interesting frequency dependence.

The purpose of this work was to gain more data on the effect of ultrasound in such photochemical reactions which can proceed *via* radicals or unstable complexes between the excited states of the reactants (excimers, exciplexes). Carbon tetrachloride was taken as an electron acceptor and the benzothiazole derivatives (Chart 1), *N*-(*tert*-butyl)benzothiazole-2-



sulfenamide (TBBS), *N*-(cyclohexyl)benzothiazole-2-sulfenamide (CBS) and 2-mercaptobenzothiazole (MBT) as the electron donors.²²

Results and discussion

In previous papers,^{23,24} we described the photolyses of several benzothiazole derivatives in methanol solution, and the structure of the products. Without sonication, photolysis generates Cl⁻ and carboxylic acids, mostly acetic acid along with C₂Cl₆, CHCl₃, CH₂Cl₂ and other partially dechlorinated materials. The structures of some of the products from the TBBS degradation (shown in Chart 2) were determined by GC-MS and comparison of their MS spectra with standards.

Francony and Pétrier have found that CCl₄ in water (*c* = 3.4 × 10⁻³ mol L⁻¹) is sonolyzed in a few hours.²⁵ It was therefore of interest to check the effect of ultrasound alone on our system, which is a solution of the donors in pure carbon tetrachloride, or to be more precise in water-saturated carbon tetrachloride

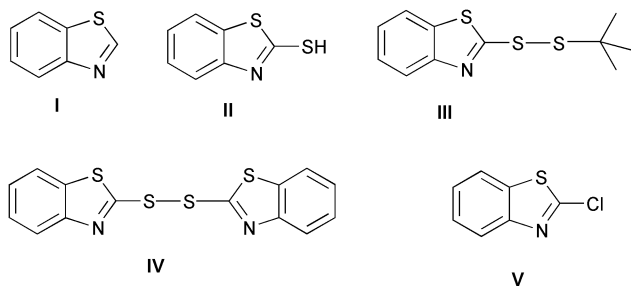


Chart 2

($c = 3.4 \times 10^{-3} \text{ mol L}^{-1}$); ultrasound does not disrupt the phase equilibria, which means that we are working with a two-phase system.

We decided therefore to pay attention in subsequent experiments mostly to the determination of C_2Cl_6 and Cl^- , which result from the degradation of the supposed exciplex or *via* CCl_3 dimerization.

In agreement with other authors,^{5,6} we admit that the excitation of the electron donor is followed by the formation of exciplexes, further transformed into an contact ion pair CIP [(electron donor)⁺-(CCl_3Cl)⁻]. Formation of a charge-transfer complex in the electronic ground state was not detected by UV-VIS spectroscopy. Ultrasound should not affect the rate of exciplex formation because CCl_4 is present in a large excess, but it could enhance the decomposition rate of CIP to ions and radicals formed from the donors and acceptors. It was proved that ultrasound in the cavitation regime can change the dielectric properties of the solvent,²⁶ which can affect the stability of exciplex(es) or ion pair(s). Ion separation by diffusion or chemical reaction of the ions produced is also influenced by the solvation.

The results of the experiment with the TBBS electron donor are depicted in Figs. 1–3.

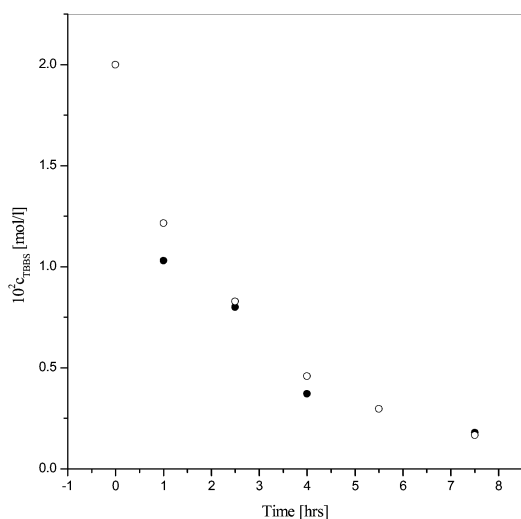
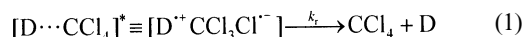


Fig. 1 [TBBS] decrease in CCl_4 solution during photolysis with (●) and without (○) sonication.

It appears clearly from Fig. 1 that ultrasound practically did not change the rate of the TBBS photolysis. This is proof of the fact that ultrasound does not influence the re-formation of either the donor or the acceptor by the reaction depicted in eqn. (1). If this were not the case, then ultrasound should



decrease the rate of donor consumption. On the other hand, the results in Figs. 2 and 3, and Table 1 show that ultrasound lowers

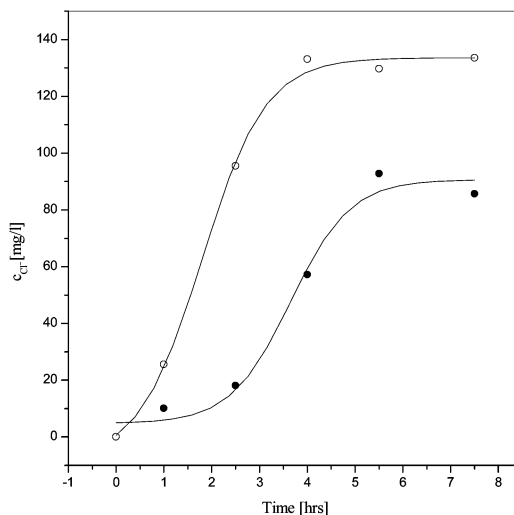


Fig. 2 Time dependence of Cl^- formation during TBBS photolysis ($c = 2 \times 10^{-2} \text{ mol L}^{-1}$ in CCl_4) with (●) and without (○) sonication.

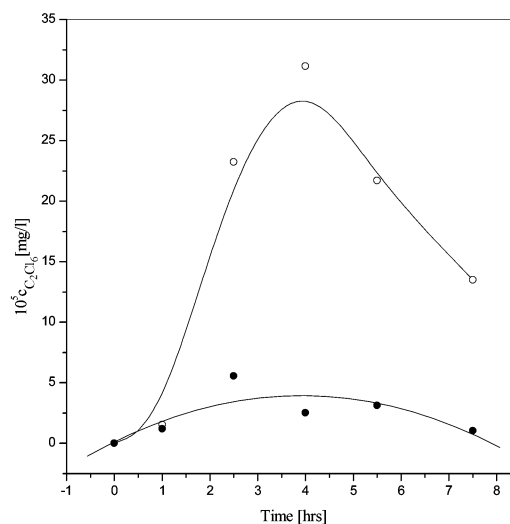


Fig. 3 Time dependence of C_2Cl_6 formation during TBBS photolysis ($c = 2 \times 10^{-2} \text{ mol L}^{-1}$ in CCl_4) with (●) and without (○) sonication.

the amount of Cl^- ions and C_2Cl_6 . The fact that a maximum appears on the latter curve demonstrates that a competitive reaction occurs in parallel, most probably the decomposition of C_2Cl_6 . This maximum is reached faster when ultrasound is applied, and the highest concentration of C_2Cl_6 is lower, because ultrasound brings about a more even distribution of the CCl_3 radicals in the whole solution which makes their dimerization less probable.

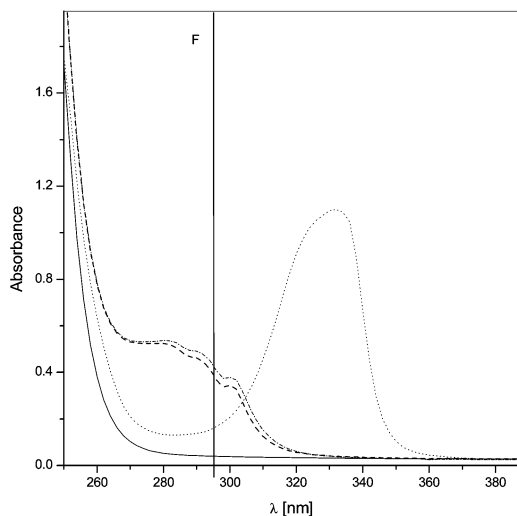
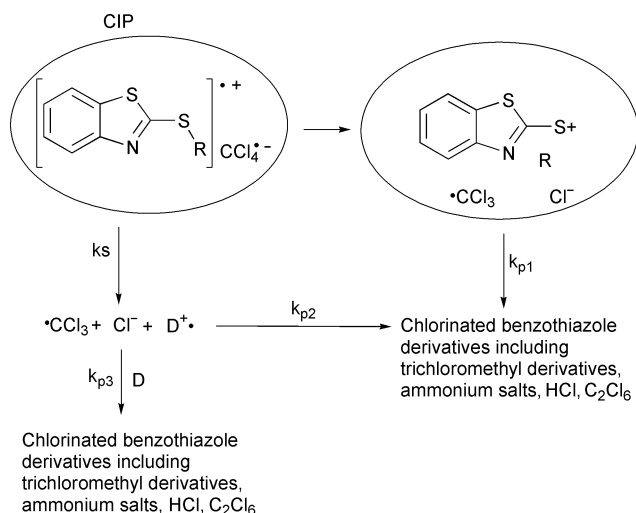
In order to explain these results it is necessary to stress that just benzothiazole derivatives (electron donors) can absorb the UV light under the experimental conditions (see Fig. 4) and that the organic solutes in CCl_4 are encapsulated in solvent cages from which they cannot escape.²⁷ We can assume that in our experiments the excited state of the electron donor inside the solvent cage can form an exciplex with the CCl_4 molecules. After electron transfer the contact ion pairs (CIP) decompose (Chart 3) in an ultrasound-insensitive unimolecular cleavage.¹⁶ Ultrasound can facilitate the access of water to the cation radical and by this means increases the probability of its fragmentation. Sonochemical destruction of CIP enables the formation of several chlorinated products inside the solvent cage. This results in a lower probability of Cl^- formation. A similar situation was observed for the photolysis of benzo-

Table 1 Results of photo- and photosono-degradation of carbon tetrachloride

t/h	TBBS				CBS				MBT			
	[Cl ⁻]/mg L ⁻¹ No))))))		10 ⁵ [C ₂ Cl ₆]/mol L ⁻¹ No))))))		[Cl ⁻]/mg L ⁻¹ No))))))		10 ⁵ [C ₂ Cl ₆]/mol L ⁻¹ No))))))		[Cl ⁻]/mg L ⁻¹ No))))))		10 ⁵ [C ₂ Cl ₆]/mol L ⁻¹ No))))))	
0	0	0	0	0	0	0	0	0	0	0	0	0
1	25	10	1	1	20	22	2	0	4	5	—	—
2.5	95	18	23	6	63	22	21	5	4	9	—	—
4	133	57	31	2	64	32	29	5	17	14	—	—
5.5	130	93	22	3	81	43	22	4	19	14	—	—
7.5	133	103	13	1	76	42	13	2	22	19	—	—

Table 2 Chlorine content (non-ionogenic materials) in the residues after evaporation of carbon tetrachloride after 7.5 h photolysis

	TBBS		CBS		MBT	
	No))))))	No))))))	No))))))
% Cl	7.51	14.11	7.33	12.03	5.06	6.49

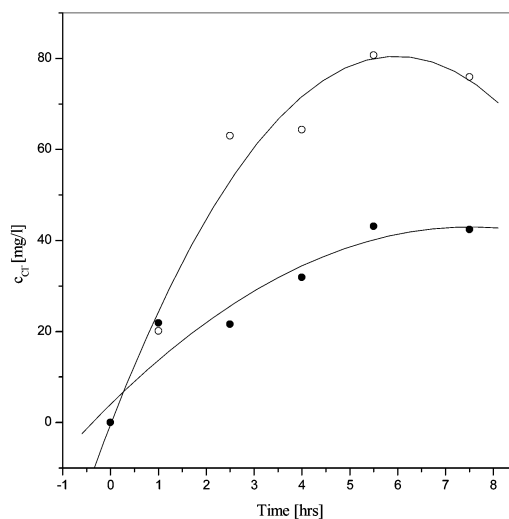
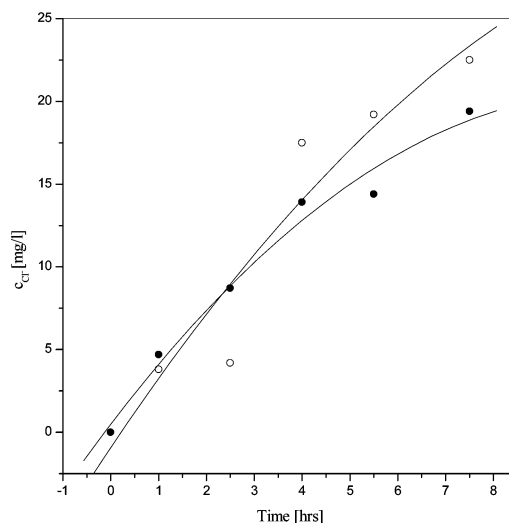
**Fig. 4** UV spectra of CBS (---), TBBS(—), MBT (· · · · ·) ($c = 2 \times 10^{-2} \text{ mol L}^{-1}$ in CCl_4) and CCl_4 ($l = 0.2 \text{ cm}$), F: optical filter.**Chart 3**

phenone in cyclodextrin (CD) complexes,²⁷ or in micellar media.²⁸ Under such conditions very effective hydrogen abstraction occurs.

Our assumption was supported by the elemental Cl analysis (Table 2) of the residues left after evaporation of the solvent (carbon tetrachloride). A higher amount of Cl was determined

in the residues from sono-photochemical experiments than from the pure photochemical experiments.

Very similar results were observed with CBS as the electron donor (Fig. 5), but with MBT the results were very different (Table 1, Fig. 6). No ultrasonic damping of the Cl⁻ formation

**Fig. 5** Time dependence of Cl⁻ formation in the photolysis of CBS ($c = 2 \times 10^{-2} \text{ mol L}^{-1}$ in CCl_4) with (●) and without (○) sonication.**Fig. 6** Time dependence of Cl⁻ formation in the photolysis of MBT ($c = 2 \times 10^{-2} \text{ mol L}^{-1}$ in CCl_4) with (●) and without (○) sonication.

rate occurred here and the C₂Cl₆ concentration was at the detection limit.

Rationalization of these results can be based on the differences in exciplex stability, which should be a function of the reducing ability of the donor. The redox potentials of TBBS and CBS should be similar, but that of MBT should differ substantially from the two others. This assumption was proved by

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

<i>E/eV</i>	TBBS	CBS	MBT (thiol)	MBT (thione)
HOMO _{S0}	-7.10	-7.12	-8.73	-8.14
LUMO _{S0}	1.75	1.73	1.59	1.44
HOMO _{S1}	-7.14	-7.16	-8.94	-8.21
LUMO _{S1}	1.78	1.75	1.62	1.49

calculations of the frontier molecular orbitals (Table 3). Thus, MBT forms too unstable an exciplex, but it can be decomposed directly by photolysis. The reaction intermediates formed in this way could produce both Cl⁻ ions as well as [•]CCl₃ radicals. Carbon trichloride radicals could abstract the hydrogen atom from MBT, forming chloroform and lowering the amount of C₂Cl₆.

The observed negative ultrasound effect could be explained also assuming that ultrasound can increase the rate of return of the excited states to the fundamental state by population of vibrational states induced by ultrasound. This could also explain the observed greater effect of ultrasound in the experiments using TBBS and CBS as the electron donors because they contain more flexible groups than MBT. Unfortunately we do not possess the necessary instruments to prove or disprove this assumption. The change of flexible SNR group for a more rigid group like phenyl would not give a clear answer to this question because the electronic effect of the substituent would be also very different.

In conclusion, sonication of a photolytic reaction implying unstable transient species such as excimers or exciplexes or ion pairs can result in a loss of efficiency, or even in the complete absence of any effect. Beyond the theoretical interest of such a conclusion, the practical consequences can be of some importance. Photolysis, with or without a catalyst, has been studied by several groups mentioned in the Introduction in attempts to decompose pollutants resistant to conventional cleaning methods. Basic research is obviously performed on simple systems containing, most of the time, only one component. Real effluents are more complex, and can contain substances liable to depress the cleavage efficiency of the actual targets. In further studies environmental chemists should exercise care in their choice of a model system, otherwise they risk finding that the proposed applications remain unfruitful.

Experimental

Materials

TBBS, CBS, and MBT were re-crystallized from ethanol or acetonitrile. Carbon tetrachloride (Lichrosolv grade, Merck Co.) was used without further purification. Redistilled water was used throughout this study.

Analytical methods

UV-VIS spectra of the samples were measured at room temperature in CCl₄ solution using a Diode Array Spectrophotometer HP 8452 A. HRGC analyses of the samples were performed on a Hewlett Packard (Palo Alto, CA, USA) 5890a Series II gas chromatograph equipped with split-splitless injector (300 °C, splitting ratio 1 : 30) and flame ionization detector operated at 300 °C. The columns used were CP-SIL 5 CB (Chrompack) cross-linked fused-silica capillary columns (10 m × 0.32 mm id) coated with 0.25 μm-thick polydimethylsiloxane. The oven temperature was programmed from 40 to 320 °C at 20 °C min⁻¹. Helium (Tatragas, 99.995%) was used as the carrier (inlet pressure 50 kPa). Air and hydrogen flow rates were 300 and 30 mL min⁻¹, respectively. The injection volume was 0.5 μL, with *n*-tetradecane or *p*-cresol as internal standards. The chromatograms were processed with an 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* 30–350 at 2.2 scans s⁻¹.

Isotachopheresis (ITP) 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, H₂O; leading anion, 10 mmol L⁻¹ nitrate; counter ion, Cd²⁺ β-alanine; additive, 0.1% w/v methyl hydroxyethyl cellulose (MHEC), pH 3.7; terminating anion, 10 mmol L⁻¹ tartrate, pH 7. Cl₂ and HClO were reduced in every sample with potassium iodide prior to ITP analysis.

Experimental set-up

All the experiments were carried out with the set-up described previously,¹⁵ consisting of a photochemical reactor equipped with a glass (SIMAX) insertion cell and an ultrasound emitter (25 kHz, 16 W cm⁻²). The UV light source was a mercury 125 W lamp from Tesla Holešovice, Czech Republic. Photo- and sono-photolyses were performed with 100 mL of 2 × 10⁻² M solutions of the appropriate electron donor in CCl₄. Water (50 mL) was added to the reaction cell (upper layer) to trap the evolved hydrogen chloride. 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 CCl₄ layers in the cell, which were analyzed by ITP (Cl⁻ and carboxylic acids) or UV-VIS (donors). The time dependence of C₂Cl₆ 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 C₂Cl₆ in carbon tetrachloride and Cl⁻ in water. All the experiments, with and without sonication, were performed under identical conditions.

Theoretical computation

The geometries of the studied molecules were optimized using the AM1 method. Energies of molecular orbitals were computed using Gaussian 98 *ab initio* HF/6-31+G** for ground states and CI/6-31+G** for excited states.

Acknowledgements

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