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PHOTODEGRADATION OF THE „NOVEL“ BROMINATED FLAME RETARDANT TRIS-(2,4,6-TRIBROMOPHENOXY)-S-TRIAZINE

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Introduction

Brominated flame retardants (BFRs) comprise a class of structurally diverse compounds that are functionally related and used in materials to reduce the flammability of polymers. Due to their global distribution, potential persistence, bioaccumulation and toxicity most of the BFRs of the first generation are banned or restricted, and replaced by new ones. However, based on similar properties these new compounds may also pose a serious risk by causing adverse effects to human health and the environment. These alternative BFRs were grouped into two classes: „novel“ and „emerging“ BFRs. Emerging BFRs are defined as compounds that have been identified in any environmental compartments whereas novel BFRs are only detected in materials and/or goods above 0.1 wt.-% [3].

The environmental fate of these alternative BFRs is partially unknown. Over the past years a multitude of studies on the photodegradation of BFRs in environmental matrices have been conducted to assess the photochemical behavior and fate in the environment [2]. The photolytic debromination reaction is particularly induced among BFRs by UV exposure.

The novel brominated triazine-based flame retardant tris-(2,4,6-tribromophenoxy)-s-triazine (TTBP-TAZ) (Table 1) is a BFR that is mainly used in acrylonitrile butadiene styrene and high impact polystyrene [3, 4].

Ballesteros-Gómez et al. detected TTBP-TAZ in 8 of 13 plastic parts of consumer products and in 9 of 17 indoor dust samples [5] but the photochemical behavior and fate is not known until now.

The results of the present study, focused on photodegradation processes were performed for the first time for TTBP-TAZ to identify the photolysis intermediates and products to assess the environmental fate.

Materials and methods

Chemicals

HPLC-grade acetonitrile and tetrahydrofuran (THF, p.A.) were purchased from Th.Geyer (Renningen, Germany). Formic acid (98-100 %) was acquired from Merck (Darmstadt, Germany). TTBP-TAZ (>98 %) was obtained from TCI Europe (Zwijndrecht, Belgium). Ultrapure water was produced by a Seralpur PRO 90 CN system (Ransbach-Baumbach, Germany).

Irradiation experiments

A water-cooled laboratory UV-reactor equipped with a 150 W medium pressure mercury lamp (TQ 150, Heraeus Noblelight, Hanau, Germany) was used for all irradiation experiments. For this irradiation studies, 200 mL of a 100 μ M solution of TTBP-TAZ in a 85 : 15 volume mixture of acetonitrile and tetrahydrofuran were placed in the reactor vessel and constantly stirred with a magnetic stirring device (600 min⁻¹). The water cooling system of the UV-reactor was set to 12.5 °C. After equilibration, the UV-lamp was activated and samples (1 mL) were collected at 0, 5, 10, 15, 20, 25, 30, 35, 40, 50 and 60 min.

Analytical methods

The primary detection after UV irradiation was monitored by high performance liquid chromatography (HPLC) analyses using an Agilent 1200 series HPLC-DAD system (Agilent Technologies, Waldbronn, Germany). The chromatographic separation was achieved using a Gemini® C18 analytical column (100 x 2 mm, 3 μ m particles; Phenomenex®, Aschaffenburg, Germany), preceded by a Gemini® C18 guard column (4 x 2 mm, 3 μ m particles). The mobile phase consisted of 0.1 % formic acid in water (A) and in acetonitrile (B). The gradient elution program was applied as follows: 0–2 min, 70 % B; 2–4 min, 90 % B; 4–6 min, 90 % B; 6–15 min, 100 % B; 15–20 min, 100 % B; 20–20.1 min, 70 % B; 20.1–30 min, 70 % B. The solvent gradient was adopted for a total run time of 30 min, while 15 min were used for column

regeneration. The flow rate was at 250 $\mu\text{L min}^{-1}$. All sample and standard solutions were injected in triplicate with an injection volume of 10 μL . The chromatograms were monitored at UV 210 nm. HPLC-MS/MS analyses were performed on an API 4000 QTrap[®] MS/MS system (Sciex, Darmstadt, Germany), equipped with electrospray ionisation (ESI) interface and hyphenated to an 1200 series HPLC system (Agilent Technologies). The chromatographic separation was performed as described above.

Results and discussion

Absorption spectrum of TTBP-TAZ measured by HPLC-DAD in acetonitrile is shown in Figure 1a with a maximum absorption wavelength for TTBP-TAZ at $\lambda_{\text{max}} = 210 \text{ nm}$. The corresponding chromatogram of TTBP-TAZ at 0 min is given in Figure 1b (blue line). In order to determine the decomposition of TTBP-TAZ further chromatograms were recorded after different irradiation times. The appearance of new peaks with different absorption spectra (data not shown) compared to TTBP-TAZ was an indicator for the formation of photo-transformation products (PTP). For TTBP-TAZ, overall nine PTPs were detected. The chromatographic behaviour demonstrated, with exception of PTP9, that all PTPs formed during the UV irradiation have probably a higher polarity than TTBP-TAZ ($R_t = 12.68 \text{ min}$), which is indicated by shorter retention times.

The relative degradation of TTBP-TAZ as a function of irradiation time is given in Figure 2a. This shows the degradation proceeded rapidly at the beginning of UV exposure so that the photochemical transformation process turned 85 % of TTBP-TAZ after 10 min into its PTPs. The formation of these compounds in correlation of TTBP-TAZ at 0 min is shown in Figure 2b. Usually, the relative peak areas of the detected products changed with the increase of irradiation time. The peak areas of PTP1 – 4 and 9 increased gradually over the course of 60 min of UV exposure whereby the peak areas of PTP5 – 8 decreased after reaching their maxima at 5 min.

Especially the peak areas of PTP6 ($R_t = 10.35 \text{ min}$) and PTP8 ($R_t = 11.34 \text{ min}$) increased between 0 and 5 min and decreased afterwards about approximately 30 % for PTP6 and approximately 50 % for PTP8. An interesting product was PTP9 because it also showed the same increase and then decreased processes like the PTP1 – 4 but PTP9 had a retention time ($R_t = 12.16 \text{ min}$) between PTP8 and TTBP-TAZ. Hence, the polarity of this product is different to the PTP1 – 4. The generation of PTPs from TTBP-TAZ is a multistage process which can be divided in two major stages: (a) direct formation of PTPs and (b) indirect formation. In the first one, the PTPs were formed directly from degradation of TTBP-TAZ. Afterwards photoPTP1 – 4 and 9 are formed from the degradation of PTP5 – 8.

The photodegradation pathway of TTBP-TAZ could not be clarified until now, but it is probable that the PTPs are formed by debromination of the aromatic system or by ether bond cleavage like it is described for DPTE and BTBPE [6]. The suggested molecular formulas of these products measured by HPLC-MS/MS are listed in Table 2. The decreasing retention time of PTP1 – 8 implies that debromination on the phenyl is a main photo transformation pathway. Due to the different polarity of PTP9 it is probable formed by ether bond cleavage but its identification is not clarified.

Hence, the identification of the formed photo-transformation products and the photochemical pathway of TTBP-TAZ will be objectives of further investigations. For this purpose the PTPs will be isolated by preparative HPLC and identified with HPLC-MS/MS, HRMS and NMR spectroscopy.

References

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Table 1. Chemical structure and main physico-chemical properties of TTBP-TAZ [3].

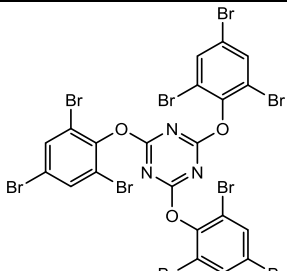
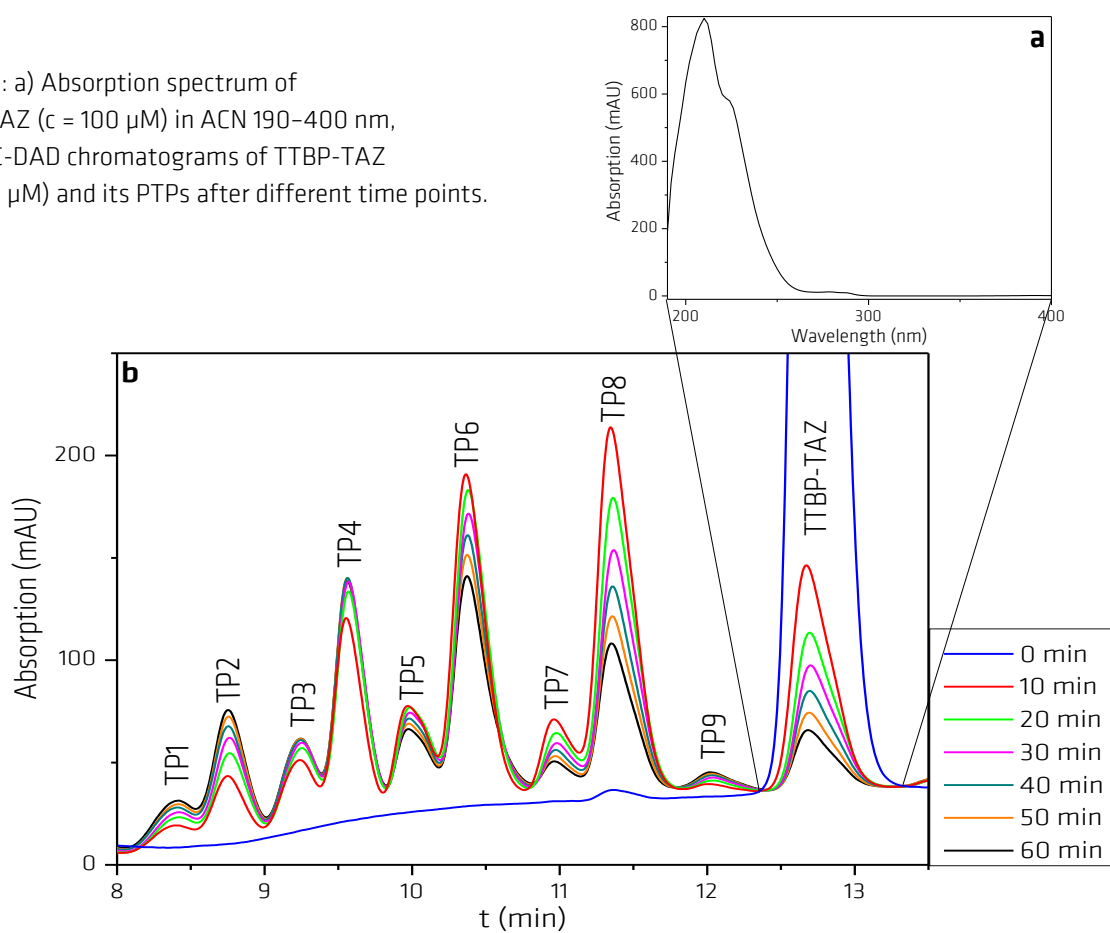
Structure	CAS no	MW	LogK _{ow}	K _{oc}	Water solubility
	25713-60-4	1067.43 g mol ⁻¹	12.97	1.0 x 10 ⁷	< 1 μg L ⁻¹ (20 °C)

Figure 1: a) Absorption spectrum of TTBP-TAZ ($c = 100 \mu\text{M}$) in ACN 190–400 nm, b) HPLC-DAD chromatograms of TTBP-TAZ ($c = 100 \mu\text{M}$) and its PTPs after different time points.



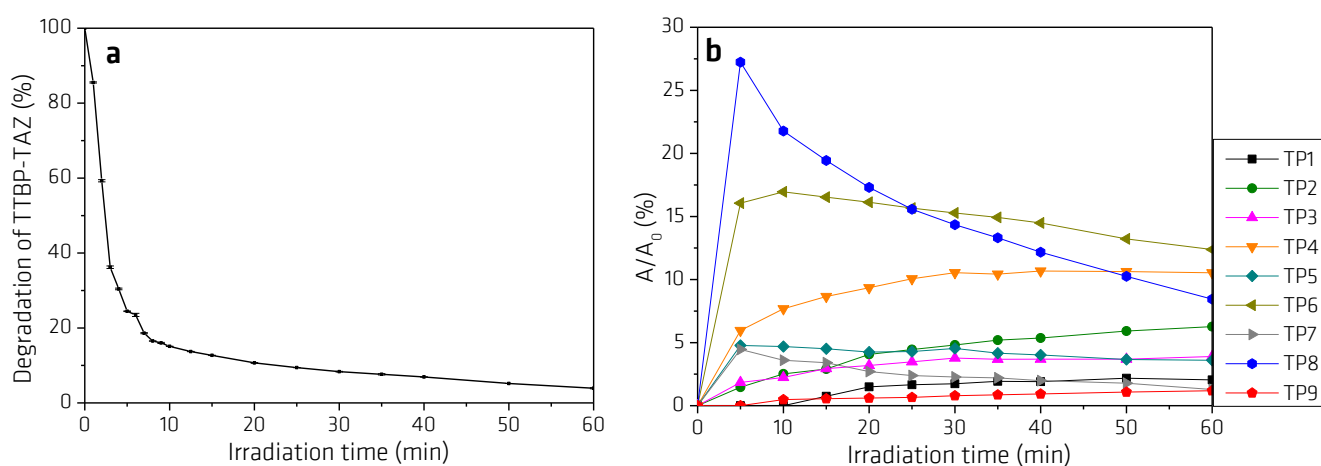


Figure 2: a) Photodegradation of TTBP-TAZ after selected irradiation times. Error bars represent the standard deviation ($m = 3$), b) Formation of PTPs of TTBP-TAZ measured by HPLC-DAD (A/A_0 as A – peak area of PTPs and A_0 – peak area of TTBP-TAZ at 0 min), (initial concentration of TTBP-TAZ = 100 μ M).

Table 2. Retention times, main ions and ion raw formulas of TTBP-TAZ and its photo-transformation products after UV irradiation (Q_1 Multiple Ion scan).

PTP	R_t (min)	m/z	Ion raw formula $[M+H]^+$
TP1	8.36	752	$C_{21}H_{11}Br_5N_3O_3$
TP2	8.75	752	
TP3	9.22	831	$C_{21}H_{10}Br_6N_3O_3$
TP4	9.53	831	
TP5	9.96	910	$C_{21}H_9Br_7N_3O_3$
TP6	10.35	910	
TP7	10.96	989	$C_{21}H_8Br_8N_3O_3$
TP8	11.34	989	
TP9	12.12	N/A	N/A
TTBP-TAZ	12.71	1068	$C_{21}H_7Br_9N_3O_3$

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