

Photodegradation of Tetrahalobisphenol-A (X = Cl, Br) Flame Retardants and Delineation of Factors Affecting the Process

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Abstract

The photoassisted degradation (HPLC-UV absorption), dehalogenation (HPLC-IC) and mineralization (TOC decay) of the flame retardants tetrabromobisphenol A (TBBPA) and tetrachlorobisphenol A (TCBPA) were examined in UV-irradiated alkaline aqueous TiO₂ dispersions (pH 12), and for comparison the parent bisphenol A (BPA, an endocrine disruptor) in pH 4 – 12 aqueous media to assess which factor impact most on the photodegradative process. Complete degradation ($2.7\text{--}2.8 \times 10^{-2} \text{ min}^{-1}$) and dehalogenation ($1.8 \times 10^{-2} \text{ min}^{-1}$) of TBBPA and TCBPA occurred within 2 hrs of UV irradiation, whereas mineralization ($2.3\text{--}2.7 \times 10^{-3} \text{ min}^{-1}$) was only 45–60% complete within 5 hrs for the flame retardants at pH 12 and ca. 80% for the parent BPA. Factors examined in the pH range 4–12 that impact the degradation of BPA were the point of zero charge of TiO₂ particles (pH_{pzc}; electrophoretic method), particle or aggregate sizes of TiO₂ (light scattering), and the relative number of •OH radicals (as DMPO–•OH adducts; ESR spectroscopy) produced in the UV-irradiated dispersion. Dynamics of BPA degradation ($2.0\text{--}2.4 \times 10^{-2} \text{ min}^{-1}$) were pH-independent and independent of particle/aggregate size, but did correlate with the number of •OH radicals, at least at pHs 4 to 8–9, after which the rates decreased somewhat at pH > 9 with decreasing adsorption owing to Coulombic repulsive forces between the very negative TiO₂ surface and the anionic forms of BPA (pK_as ca. 9.6–11.3), even though the number of •OH radicals continued to increase at the higher pHs.

Keywords: Tetrabromobisphenol-A; Tetrachlorobisphenol-A; Bisphenol-A; Dehalogenation; TiO₂-assisted photodegradation; Mineralization

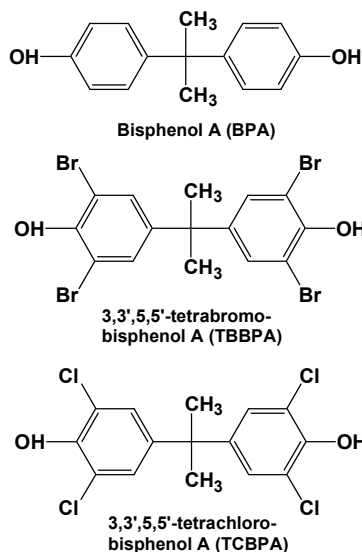
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1. Introduction

Tetrabromobisphenol-A {TBBPA; 4,4'-isopropylidenebis(2,6-dibromophenol)} is a flame retardant used extensively in the treatment of paper, textiles, plastics, circuit boards, carpets, upholstery, and in many other consumer goods [1–3]. The chloro analog (viz., tetrachlorobisphenol-A; TCBPA; 4,4'-isopropylidenebis-(2,6-dichlorophenol)), also a flame retardant, is used to a lesser extent as an additive in polymers (e.g. ABS), epoxy and polycarbonate resins, high impact polystyrene, phenolic resins, and adhesives [2]. World production of TBBPA stands at ca. 130,000 tons annually, of which more than 86 % of it was used in Asia alone in 2002 [4]. TBBPA is a nonvolatile and a non-mobile agent in soils partially because of its limited water solubility (\leq ca. 1 mg L^{-1} at pH ca. 7; $\log P_{\text{ow}} =$ ca. 5.9) [4], such that it and its TCBPA analog adsorb extensively on soil sediments and organic matter. At higher pHs water solubility is significantly increased causing these flame retardants to leach out into ground waters: for TBBPA, up to 630 ng L^{-1} from various landfills for the raw leachate and up to 110 ng L^{-1} for the treated leachate [5]. Others reported TBBPA levels as high as $100 \text{ } \mu\text{g Kg}^{-1}$ weight [6] and amounts up to 220 ng g^{-1} wet weight in some 116 samples of sewage sludge from 22 municipal wastewater treatment plants [7]. By contrast, the parent bisphenol-A (BPA) leaches out from polycarbonate tubes at 0.8 ng day^{-1} and in seawater at $\sim 11 \text{ ng day}^{-1}$ under controlled conditions, with the processes being pH-dependent and dose-dependent [8]. In river sediments (soil) TBBPA is toxic to fish life (e.g. to European flounder [9]).

Fires and runaway events involving these flame retardants pose further threats to the environment because of the possible release of hazardous decomposition byproducts such as HBr, brominated bisphenols (BPAs) and brominated phenols, among others, for TBBPA in an open reactor [10, 11]. In contaminated sediments, TBBPA is debrominated to bisphenol-A anaerobically by microorganisms passing through the tri-, di- and mono-brominated BPA stages, with 2,2'-dibromobis-

phenol-A being the dominant metabolite [12]. By contrast, BPA persists under anaerobic conditions but does biodegrade aerobically to 4-hydroxybenzoic acid and 4-hydroxyacetophenone [13].



The ubiquitous presence in the environment and its exposure to humans has made bisphenol-A the object of intensive scrutiny. This endocrine disruptor is produced in large quantities worldwide (e.g. ca. 590,000 tons in Japan in 2004 [14] and ca. 723,000 tons in the United States annually [15]) and is widely used in the production of epoxy resins and polycarbonate plastics. Not surprisingly, significant quantities of BPA leach out into seawater from polycarbonate tubes at 37°C, particularly relevant in tropical zones and sea coasts during the summer months [8].

Studies on the toxicity of these flame retardants (*in vitro* assays) indicate that TBBPA is a 25-fold more potent binder onto human transthyretin (the thyroid transport protein) than is the native hormone thyroxin [16]. For BPA and related compounds, *in vitro* and *in vivo* reporter assays by Kitamura and coworkers [17] established the estrogenic activity of these compounds in human breast cancer cell line MCF-7, with TCBPA exhibiting the highest activity followed by bisphenol-B and bisphenol-A. The latter interferes with the endocrine system, disrupts physiologic functions, and stimulates androgen- independent proliferation of prostate cancer cells [18], and not least BPA can trigger human breast cancer [19].

Treatment of wastewaters containing TBBPA along with the chloro analog and bisphenol-A is an important issue in the remediation of aquatic ecosystems. Accordingly, the photoassisted degradation, dehalogenation and mineralization of these halogenated substrates were examined in alkaline TiO₂ dispersions (pH 12), a medium in which they are soluble. The present study also examined the influence of the halogen substituents (Br and Cl) on TBBPA and TCBPA in the photodegradative process, since halide (Br⁻ and F⁻) ions are known to interfere in the photodegradation of halophenols [20]. The highly water-soluble endocrine disruptor BPA was examined in the pH range 4–12 to assess which factors of the metal-oxide TiO₂ (particle or aggregate size, surface charge and number of •OH radicals produced) impact the degradation dynamics.

2. Experimental Section

2.1 Chemical reagents

Degussa P-25 TiO₂ was supplied by Nippon Aerosil Co. Ltd. {particle size, 20–30 nm (TEM); ca. 83 % anatase and 17% rutile (XRD); surface area, 53 m² g⁻¹ (BET)}. High purity grade bisphenol-A, tetrachlorobisphenol-A and tetrabromobisphenol-A substrates were supplied by Tokyo Kasei Co. Ltd.

2.2 Photodegradation Procedures

An aqueous solution (ion-exchanged water) of BPA, TBBPA or TCBPA (0.10 mM, 50 mL) and TiO₂ (30 mg) contained in a 120-mL closed Pyrex reactor was adjusted to pH 12 with NaOH; at lower pHs, TBBPA and TCBPA are not soluble. The TiO₂/substrate suspension was dispersed by sonication for ca. 3 min and then purged for 10 min with oxygen gas under dark conditions prior to UV irradiation with a 75-Watt high-pressure Hg lamp (ca. 0.8 mW cm⁻²; wavelength range, 320–390 nm; maximal emission, λ = 360 nm) under continuous magnetic agitation. The irradiated dispersion was sampled at various time intervals (up to 300 min), followed by filtration through a Dismic 0.20 μm syringe filter and centrifugation for 10 min. For comparison, a TiO₂/BPA aqueous dispersion was also examined at pHs 4.0 to 12.0 under otherwise identical experimental conditions.

2.3 Analytical methods and procedures

The time profiles of the degradation of BPA, TBBPA and TCBPA were obtained by monitoring concentration changes using a JASCO liquid chromatograph (HPLC) equipped with a JASCO UV-2070 UV/Vis diode array multi-wavelength detector and a JASCO Crestpak C-18S column; the eluent was a mixed solution of ethanol/water (9:1 v/v ratio). Temporal changes in total organic carbon (TOC) were assayed with a Shimadzu TOC-5000A analyzer, whereas dehalogenation of TBBPA and TCBPA was assayed by ion chromatography using a JASCO LC-2000+ HPLC chromatograph equipped with a conductivity detector and an I-524 anionic column.

Changes of the zeta-potential at the water/TiO₂ interface at various pHs were measured with an Otsuka Electronics Co. Ltd. ELS-Z2 zeta-potential analyzer using an electrophoretic technique (P-25 TiO₂, 10 mg; ultrapure water, 5.0 mL). Formation of •OH radicals during the TiO₂ photoassisted processes (oxidations or reductions) driven by UV irradiation (irradiance ca. 2.5 mW cm⁻² at 360 nm) of an aqueous TiO₂ dispersion (no substrates present) at pHs 4.0 to 12.0 was probed by ESR techniques employing the DMPO spin-trap agent (P-25 TiO₂, 10 mg; ultrapure water, 1 mL; DMPO, 0.10 mL). The intensity increase of the DMPO-•OH ESR signature was estimated relative to a standard Mn²⁺ marker using the appropriate software of the JEOL FA100 ESR spectrometer. Changes in the distribution of TiO₂ particle sizes (or aggregate size) in several dispersions (no substrates present) was also examined in the same pH range by dynamic light scattering with the Otsuka Electronics Co. Ltd. ELS-Z2 light scattering apparatus (TiO₂, 10 mg; ultrapure water, 5.0 mL); pH control of the dispersions for all the analyses used either HCl and NaOH as required.

3. Results and discussion

3.1 Photodegradation of the bisphenols

The scant water solubility of TBBPA at pHs 5 to 9 {0.148 mg L⁻¹ (pH 5), 1.26 mg L⁻¹ (pH 7), 2.34 mg L⁻¹ (pH 9) [21]; log P_{ow} = 4.5–5.3 [2]}, and TCBPA, necessitated greater alkalinity of the

aqueous medium, namely pH 12 to examine their degradation by the TiO₂ photoassisted process. By contrast, BPA is fairly soluble at all pHs (300 mg L⁻¹ [22]; log P_{ow} = 3.32 [23]).

Temporal changes in the concentration of BPA (absorption band at 224 nm), TBBPA (204 nm) and TCBPA (201 nm) resulting from the breakup of the aromatic ring at pH 12 are illustrated in **Figure 1a**. Relevant first-order kinetics are reported in **Table 1**. Within experimental error, no difference in the degradation dynamics was observed for the three bisphenols at pH 12 and at pH 6 for BPA. The Br and Cl substituents on the BPA rings enhanced the rates somewhat relative to the parent BPA substrate ($2.2 \times 10^{-2} \text{ min}^{-1}$ versus $2.7\text{--}2.8 \times 10^{-2} \text{ min}^{-1}$). Similarly, no significant changes were evident in the photoassisted mineralization kinetics of the bisphenols at pH 12 (**Figure 1b**). Regardless of the nature of

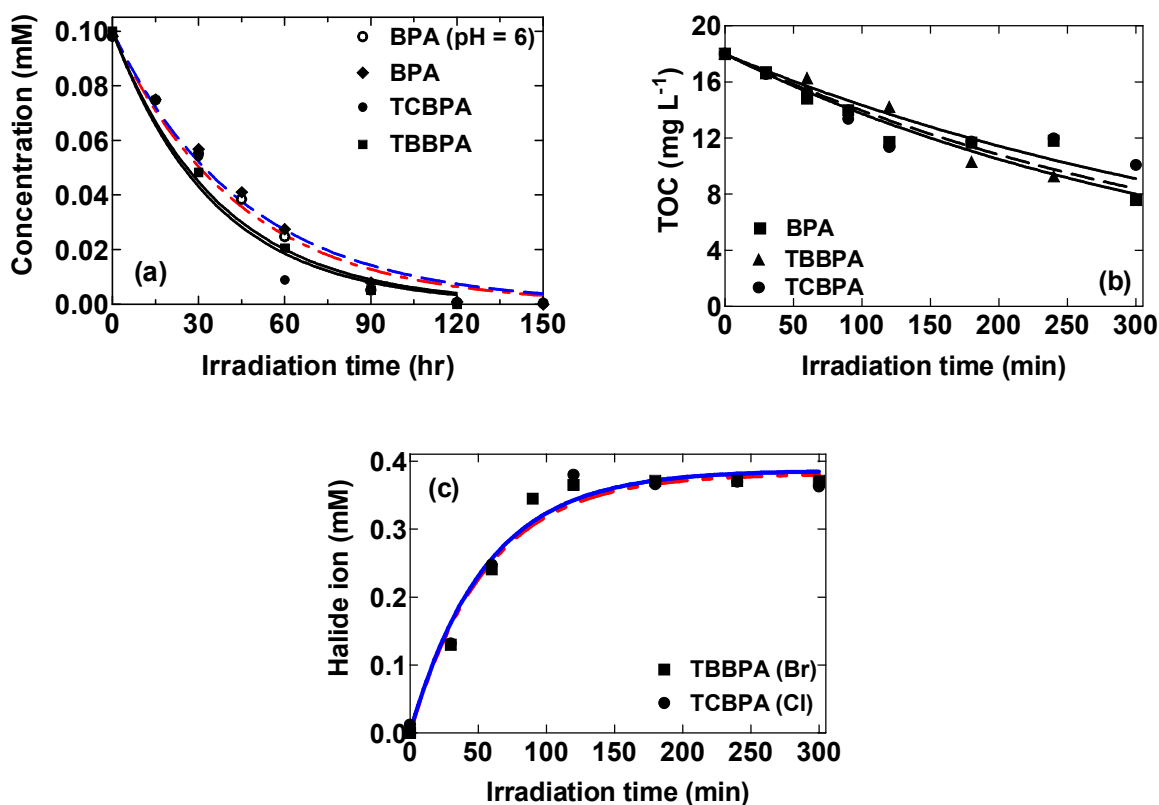


Figure 1. (a) Temporal decrease of the concentration of BPA, TBBPA and TCBPA at pH 12 by the HPLC-UV absorption technique. (b) Temporal loss of total organic carbon (TOC) during the photomineralization of BPA, TBBPA and TCBPA substrates also at pH 12. (c) Formation of Cl⁻ and Br⁻ ions during the course of the photoassisted dehalogenation of TCBPA and TBBPA.

the halo substituents, dehalogenation rates of TBBPA and TCBPA (**Figure 1c**) were identical ($1.8 \times 10^{-2} \text{ min}^{-1}$) but slightly slower than photodegradation. Nonetheless, dehalogenation was nearly complete within 2 hrs of irradiation. Evolution of CO_2 (loss of TOC) was an order of magnitude slower than degradation, that we attribute to the formation of slow degrading intermediates.

Table 1. First-order kinetics of degradation, mineralization and dehalogenation of BPA, TCBPA and TBBPA in alkaline media and extent of mineralization and dehalogenation after 300 min of irradiation.

Parameters	pH = 12		
	BPA	TBBPA	TCBPA
$k_{\text{deg}} (10^{-2} \text{ min}^{-1})$	2.16 ± 0.13	2.67 ± 0.16	2.80 ± 0.40
$k_{\text{min}} (10^{-3} \text{ min}^{-1})$	2.5 ± 0.2	2.7 ± 0.2	2.3 ± 0.3
% mineralization (TOC loss)	58	58	44
$k_{\text{X}} (10^{-2} \text{ min}^{-1})$	---	1.8 ± 0.2	1.8 ± 0.3
% X produced (X = Br or Cl)	---	97	96

In summary, degradation through ring opening and dehalogenation processes are fairly prompt in alkaline media occurring within 2 hrs of irradiation. By contrast, mineralization of BPA, TBBPA and TCBPA is a slower process attaining only ca. 45–60% completion after a 5-hr irradiation period at pH 12. Mineralization of BPA in neutral media was ca. 80% complete within the same period.

3.2 Possible factors impacting the photodegradation of bisphenols

In general, photoassisted degradation and mineralization processes are affected by several experimental factors not least of which are (a) the wavelengths of irradiation and light irradiance, (b) the surface area, i.e. the TiO_2 particle size (aggregate size), (c) the solubility of the organic substrates in the aqueous medium, (d) the TiO_2 crystalline structure (anatase *versus* rutile), (e) the concentration of dissolved oxygen, (f) the effects of surfactant on the adsorption of pollutants on the TiO_2 particle surface (zeta-potentials and affinity), and (g) the number of $\bullet\text{OH}$ radicals produced, the major oxidizing agent on the surface of the TiO_2 upon UV irradiation. Herein we determined (i) the surface charge of TiO_2 at various pHs (zeta potentials) to assess the adsorption of the substrates on the TiO_2 particle

surface, (ii) the relative number of $\bullet\text{OH}$ radicals produced during the UV irradiation of TiO_2 in aqueous media at several pHs (4.0 to 12.0), and (iii) the size of the TiO_2 particle aggregates (hence surface area) with changes in the acidity/alkalinity of the aqueous medium.

The initial photodegradative steps depend on whether and the extent to which the bisphenols are adsorbed on the TiO_2 surface, which in turn depends on the surface charge (zeta-potentials) of the particles and the related point charges of the atoms in the bisphenols [24]. The pH-sensitive zeta potentials of aqueous TiO_2 dispersions at several pHs are reported in **Figure 2a**. The point of zero charge (pzc) of the TiO_2 particle surface in water under dark conditions occurred at pH_{pzc} ca. 6.6, whereas at pH 12.0 the zeta potential was highly negative, ca. -30 mV. At this pH the phenolic C–OH functions of BPA ($\text{pK}_{\text{a}s}$ 9.59–11.30 [25]), TBBPA ($\text{pK}_{\text{a}1} = 7.5$, $\text{pK}_{\text{a}2} = 8.5$ [6]) and TCBPA ($\text{pK}_{\text{a}s}$ similar to TBBPA) are

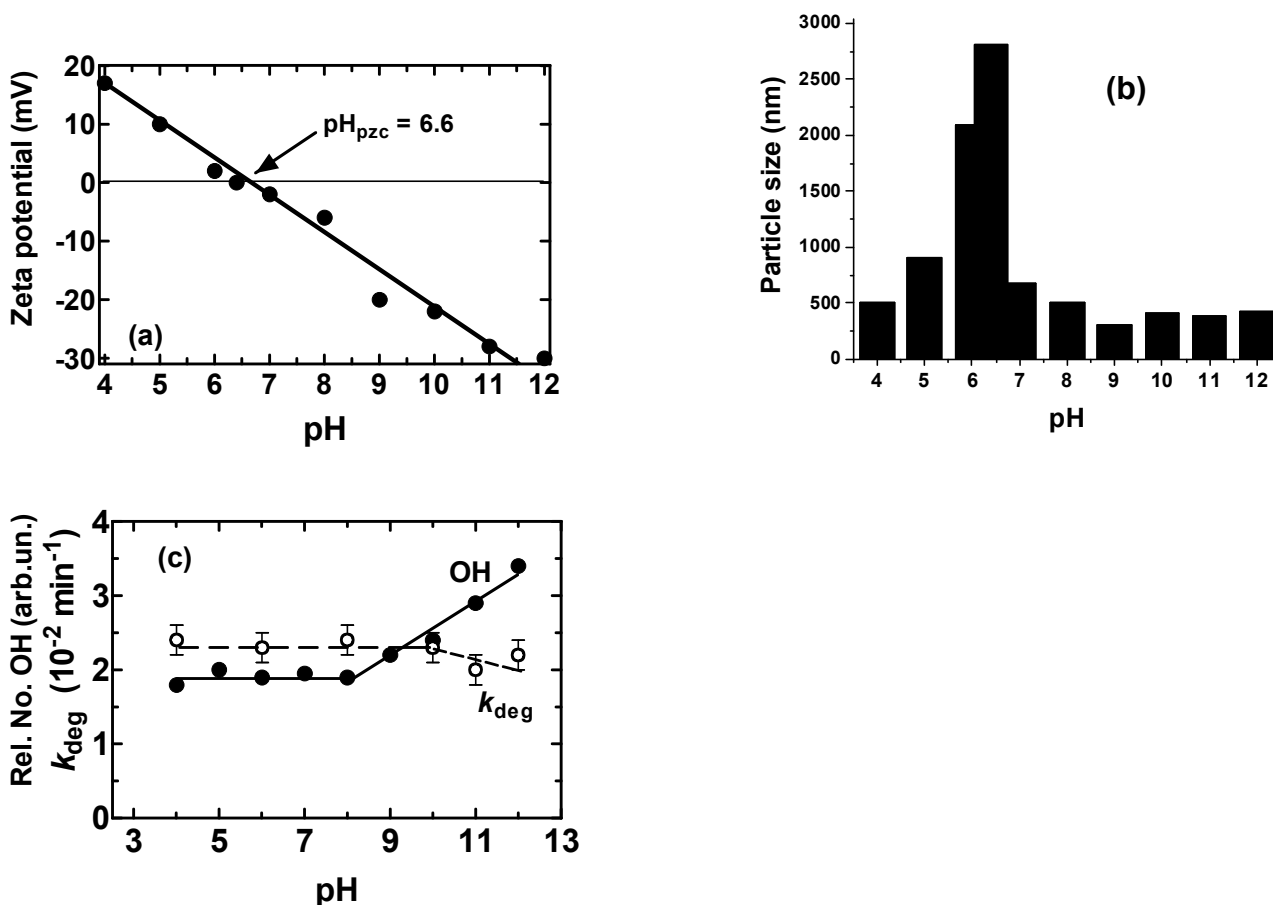
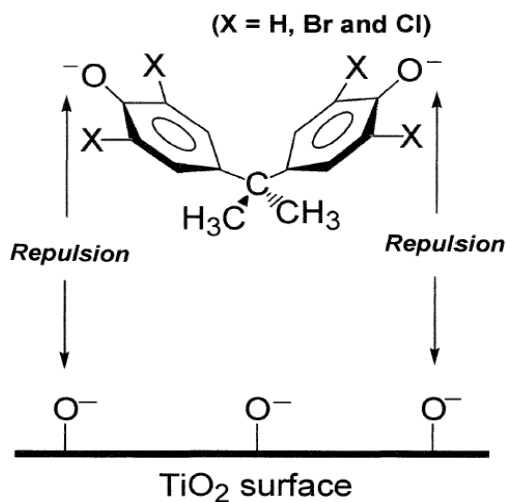


Figure 2. (a) Plot illustrating the pH-sensitive zeta potentials of aqueous TiO₂ dispersions at several pHs; (b) Size distribution of TiO₂ particle aggregates at various pHs in aqueous dispersions; (c) Comparison of the relative number of •OH radicals formed and the kinetics of photodegradation of bisphenol-A as a function of pH.

deprotonated into C–O[−] moieties so that the bisphenols are repelled by Coulombic forces by the negatively charged TiO₂ surface via the phenoxy functions. UV irradiation of the suspensions had relatively little effect on pH changing rather negligibly below pH 12. Accordingly, the substrates can only approach the metal-oxide surface through the methyl groups as portrayed in **Scheme 1**. No adsorption of the bisphenols was observed under dark conditions on the negative TiO₂ surface because of the hydrophobic nature of the methyl groups and the super-hydrophilic TiO₂ surface [26]. Consequently, we deduce that the lack of adsorption impacted negatively on the photodegradation of the bisphenols in the highly alkaline media.



Scheme 1. Proposed orientation of the bisphenols (X = H, Cl, Br) relative to the negatively charged TiO₂ surface under alkaline conditions.

Another factor that impacts the TiO₂ photoassisted degradation/mineralization of bisphenols specifically, and organic pollutants in general, is the surface area of the metal-oxide photomediator. Transmission electron microscopy (TEM) of Degussa P-25 TiO₂ particles have shown the sizes of the primitive crystallites to lie around 20–30 nm (dia.). By contrast, dynamic light scattering of aqueous TiO₂ dispersions at various pHs (**Figure 2b**) revealed aggregate size distributions of TiO₂ particles

around 500 nm in acidic media (pH 4), increasing nearly sixfold to ca. 2810 nm at the pH_{pzc} of 6.6 followed by a sharp drop at pH 7, above which the average aggregate size remained around 430 nm. The smaller aggregate sizes in acidic and alkaline media are due to Coulombic repulsions between the positively (acidic) and negatively (alkaline) charged particles, respectively, whereas the sudden increase at the pH_{pzc} is due to an intrinsic attraction between neutral particles. Evidently, the pH-dependent sizes of the TiO_2 aggregates, which reflect the area of the TiO_2 surface on which the photoinduced processes take place, play a negligible (if any) role in the photoassisted degradation and in the mineralization of the bisphenols (compare k_{deg} data of **Figure 2c** for BPA with the histograms in **Figure 2b**).

Figure 2c displays the relative number of $\bullet\text{OH}$ radicals (with respect to the standard Mn^{2+} marker) in aqueous TiO_2 dispersions in the pH range 4–12 determined from the ESR spectral signature of the $\text{DMPO}\text{-}\bullet\text{OH}$ adducts. The number of $\bullet\text{OH}$ radicals formed was relatively constant (ratio ca. 2) up to ca. pH 8, after which it increased dramatically by nearly 175% at pH 12 (ratio ca. 3.5). Under our experimental conditions, the degradation dynamics of BPA correlate with the number of $\bullet\text{OH}$ radicals so formed up to ca. pH 8–9, after which they digress which we attribute to the lack of adsorption of the substrate on the TiO_2 surface (see above). Clearly one factor, namely the increased number of $\bullet\text{OH}$ radicals with pH, is significantly attenuated by the adsorption factor.

Contrary to the present observations, a study of the pH dependence of the degradation dynamics of BPA (k_{deg}) reported by Wang and coworkers [27] showed an overall increase in the degradation rates in the pH range 3–12 from ca. $1.1 \times 10^{-2} \text{ min}^{-1}$ at pH 3 to ca. $2.5 \times 10^{-2} \text{ min}^{-1}$ at pH 12 which they inferred to be due to an increase in the number of $\bullet\text{OH}$ radicals [27]. Differences in the rates reported in **Table 1** for BPA with those of Wang et al are due to the different experimental conditions used {100% anatase TiO_2 ; 10–20 nm particles; TiO_2 loading, 1 g L^{-1} ; air-purged dispersions; BPA concentration, 0.044 mM; metal halide 250-W lamp at wavelengths $\geq 365 \text{ nm}$ }. The pH-dependent initial rates of the photoassisted degradation of 2-naphthol in aqueous TiO_2 dispersions

{conditions: Degussa P-25 TiO₂ loading, 1 g L⁻¹; concentration of 2-naphthol, 0.5 mM; air-equilibrated dispersions; irradiation wavelengths ≥ 340 nm [28]} also correlate with the pH-dependent formation of •OH radicals of **Figure 2c**. Note that both the initial concentrations of substrates and the light irradiance have a significant impact on the degradation dynamics [29].

No attempt was made in this study to examine the mechanistic details of the degradation of the tetrahalobisphenol-A substrates, nor was any attempt made to identify intermediates. Nonetheless, it is relevant to note that degradation can occur *oxidatively* by •OH radical attack on the phenyl groups and *reductively* by (TiO₂ conduction band) electron attachment to the phenyl groups as reported earlier by us for some halophenols [30]. Future studies will attempt to delineate the extent to which these two possibilities contribute to the overall photodegradation of the TBBPA and TCBPA flame retardants.

Suffices to note that for bisphenol-A, previous studies by us [24, 31] and others [27, 32, 33] that involved TiO₂ to degrade and mineralize the BPA toxin in acidic and neutral media reported various phenolic and aliphatic intermediates toward its complete decomposition to carbon dioxide. For instance, Wang and coworkers [27] noted that dissolution of BPA into the β-cyclodextrin cavity enhanced its adsorption on TiO₂ and increased the photodegradation efficiency (maximal at pHs 6–8) which decreased sharply in more alkaline media (pH 11–12). Other studies in homogeneous phase showed conversion of BPA to hydroxylated BPA-*o*-catechol and its oxidized form (BPA-*o*-quinone) by the Fenton process (H₂O₂ + FeCl₃·6H₂O in acidic media) that involves •OH radicals as the oxidative entities [8], whereas electrochemical oxidation of BPA in acidic saline (NaCl) aqueous media produced no less than 28 intermediates, many of which were chlorinated: TCBPA derivatives, together with 2,6-dichloro-*p*-benzoquinone and 2,4,6-trichlorophenol predominated [34]. By contrast, sonochemical degradation in the presence of O₂ converted BPA into 2,3-dihydro-2-methylbenzofuran, a typical BPA intermediate produced by •OH radical attack [35].

4. Concluding remarks

To summarize, the TBBPA and TCBPA flame retardants can be photodegraded and dehalogenated completely in UV-irradiated alkaline (pH 12) TiO₂ dispersions in less than 2 hrs, whereas mineralization to carbon dioxide after 5 hrs accounted only for ca. 45-60% completion. The degradation dynamics for the parent substrate BPA did not correlate with the TiO₂ particle/aggregate size at the various pHs examined (pH 4.0 to 12.0), but did correlate with the number of •OH radicals produced, at least in the range of pH from 4.0 to ca. 8.0–9.0. In more alkaline media (pH > 9), the positive impact of •OH radicals on the dynamics was strongly offset by the lack of adsorption of the BPA on the TiO₂ particle surface owing to Coulombic repulsion between the highly negative metal-oxide surface (zeta potentials) and the anionic forms of the bisphenol-A.

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