Carbon and hydrogen isotope fractionation of phthalates during photocatalysis reactions in aqueous solution containing Fe(III) complexes or iron minerals

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Content (8 pages)

1. Speciation of Fe(III) aqua complexes at different pH level and UV-vis absorption spectra of aqueous Fe(III)-complexes in aqueous solution

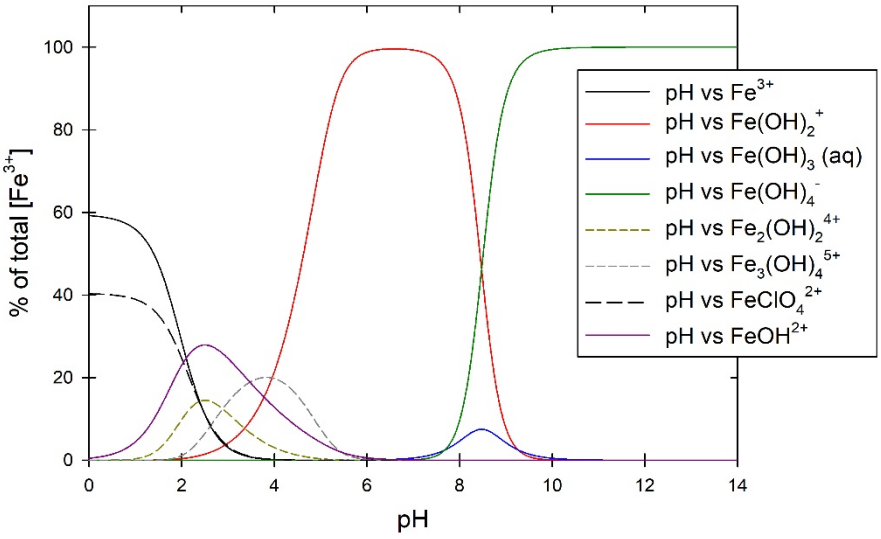


Figure S1. Speciation of Fe(III) aqua complexes at different pH level determined by Visual MINTEQ for a concentration of 0.1 M $Fe(III)(ClO_4)_3$. At pH 7 the Fe^{3+} is present with 99.3% as $Fe(OH)_2^+$, 0.5% $Fe(OH)_3$, 0.1% $Fe(OH)_4^-$, and 0.1% $Fe(OH)^{2+}$.

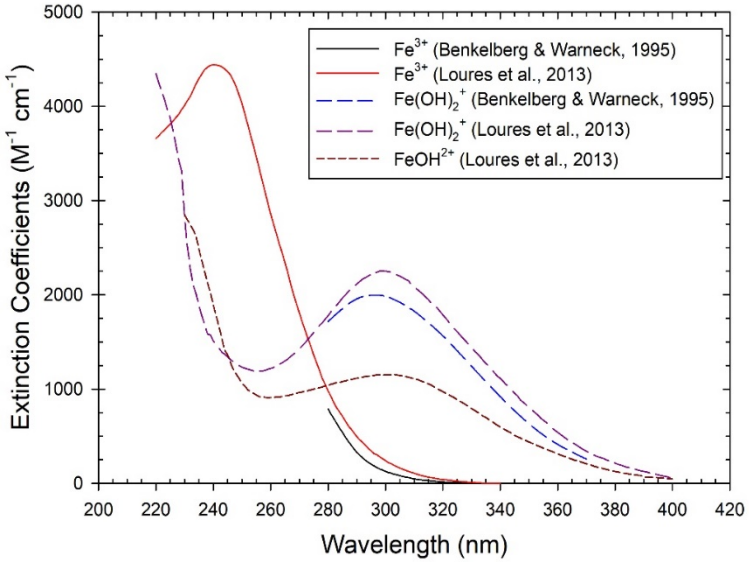


Figure S2. UV-vis absorption spectra of aqueous Fe(III)-complexes in aqueous solution. Fe^{3+} corresponds to the iron(III)-hexa-aquo complex (ferric ion), $FeOH_2^+$ is the iron(III)-tetra-aquo-dihydroxy complex and $FeOH^{2+}$ is the iron(III)-penta-aquo-monohydroxy complex (Loures et al., 2013, Benkelberg and Warneck, 1995).

2. Experimental setup for photocatalytic degradation reactions and light spectrum of the xenon lamp

Photo-induced degradation reactions of DMP, DEP and DBP were performed in a 300 mL Pyrex cylindrical flask with a quartz window (Figure S3). The solution was magnetically stirred during the whole reaction process.

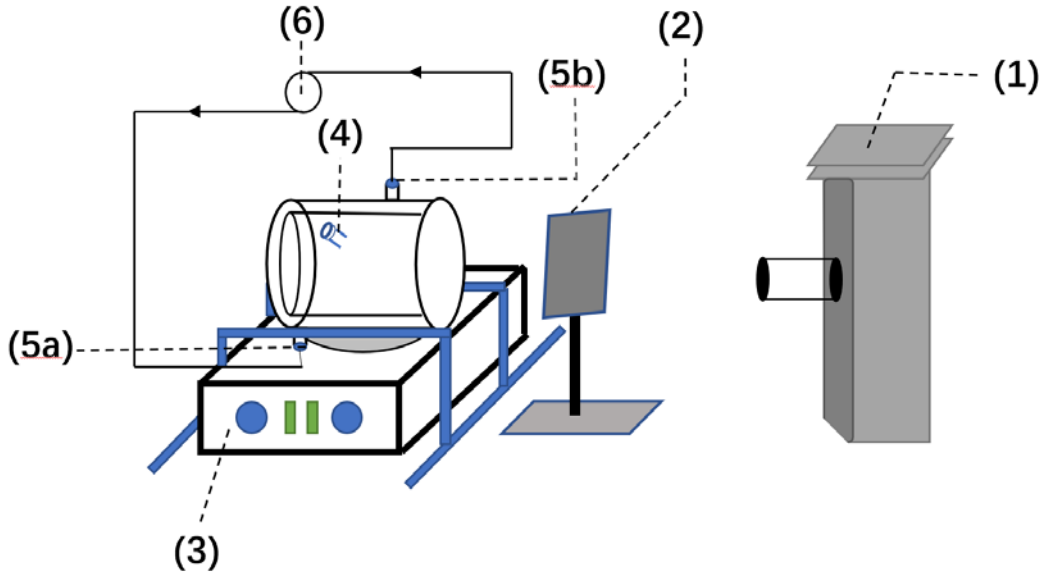


Figure S3. Experimental setup for photocatalytic degradation reactions. (1) 150W xenon lamp; (2) filter (280 nm cutoff wavelength); (3) magnetic stirrer; (4) reactor; (5a) and (5b) inlet and outlet of cooling water; (6) cooling water system

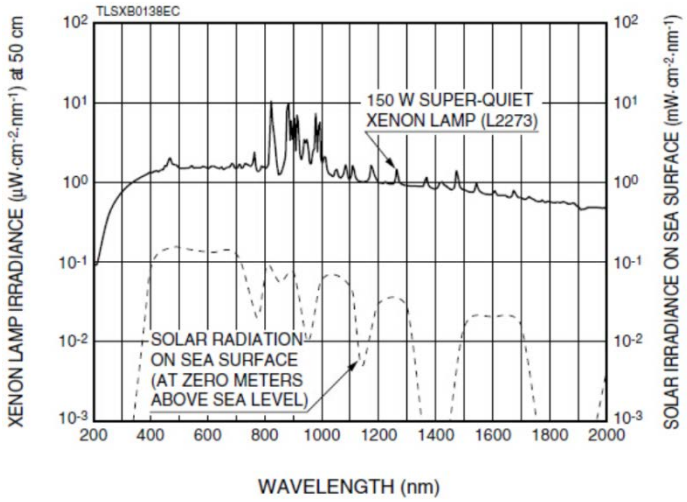


Figure S4. Light spectrum of the xenon lamp (Type L2175, Wavelength: 185-2000 nm, Hamamatsu Photonics K.K., Japan).

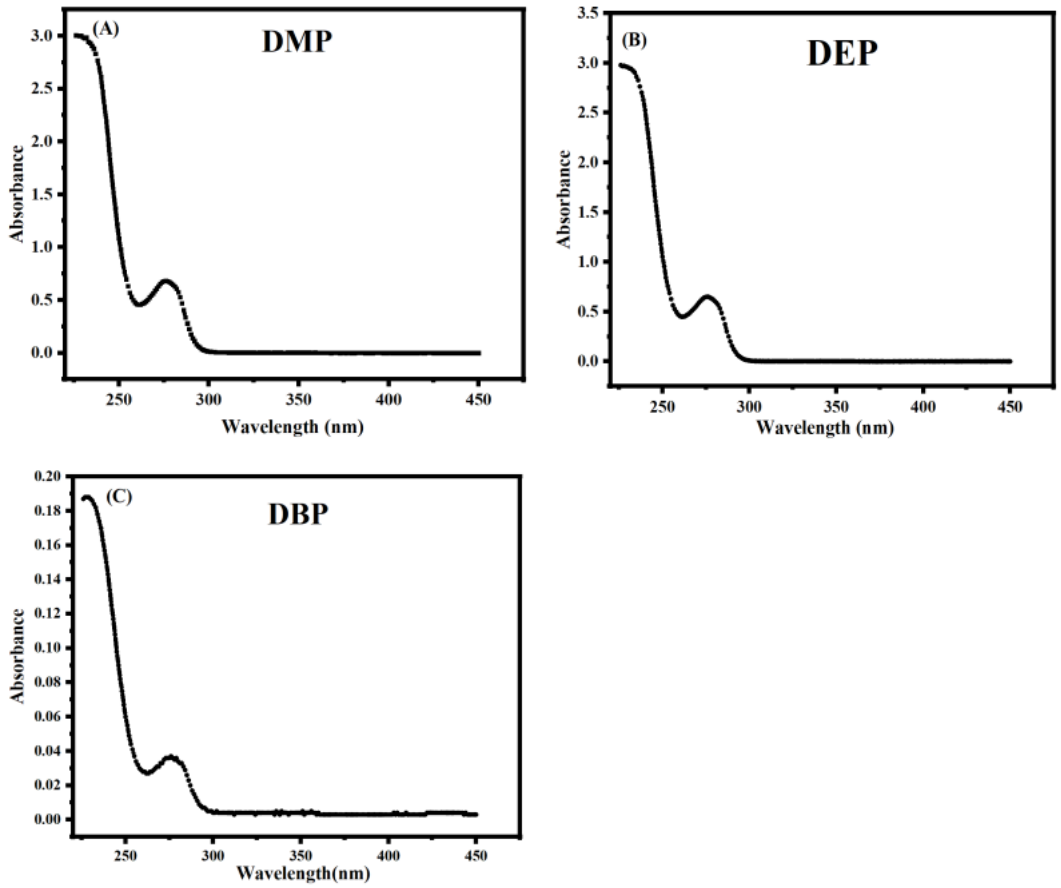


Figure S5. UV absorption spectrum of DMP (1.0 mM), DEP (0.8 mM) and DBP (0.037 mM) in water at pH 7.

3. Control experiments

Control experiments have been conducted at pH = 7 without the addition of a photo-catalyst (Fe(III) or minerals), but with UV irradiation and with the addition of a photo-catalyst (Fe(III) and minerals), but without any irradiation of the reaction solution (incubation in the dark). The remaining fraction of PAEs showed no obvious decrease in concentration and no significant carbon and hydrogen isotope fractionation over the time course of the experiments (Figure S6; Figure S7).

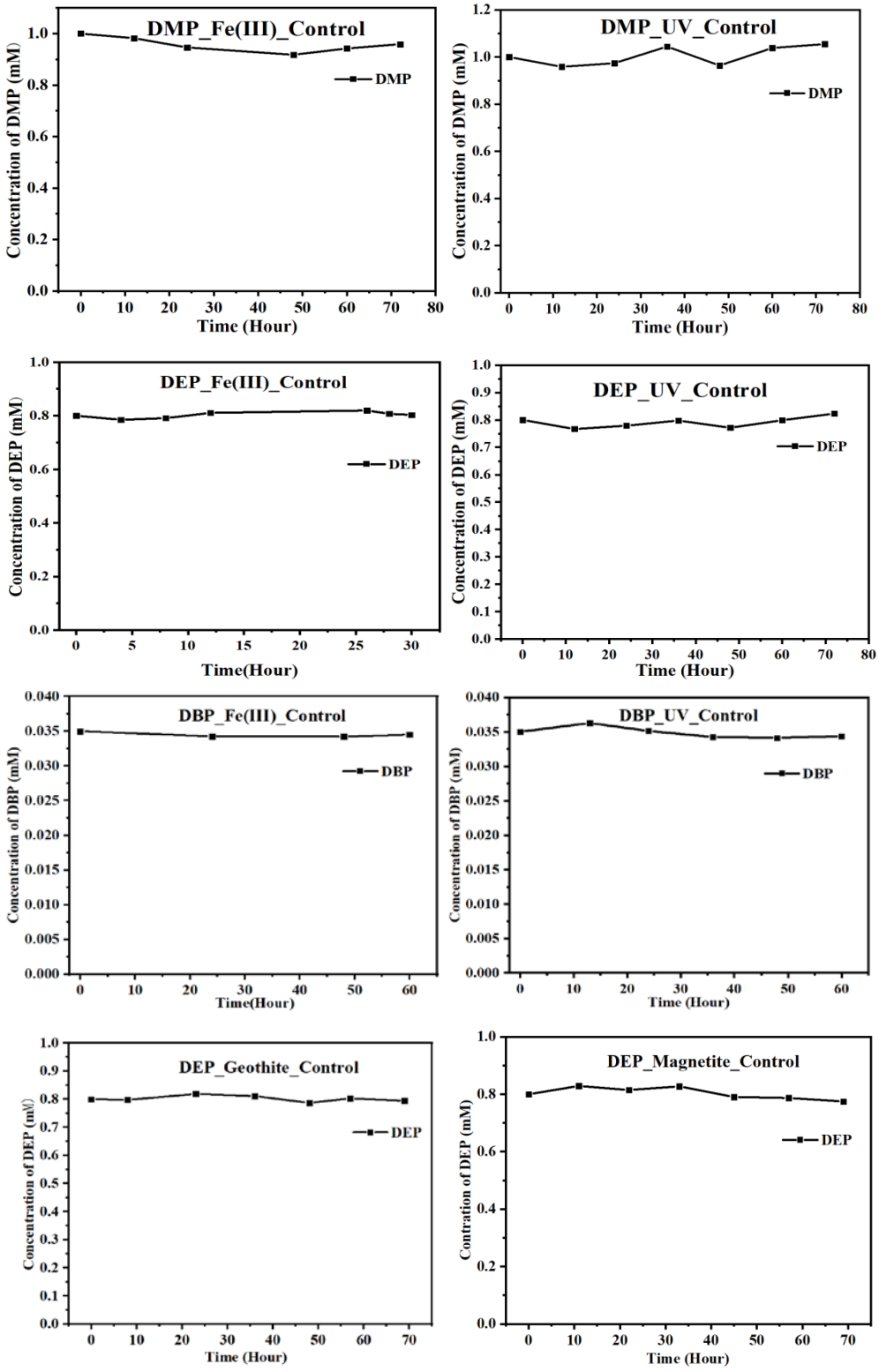


Figure S6. Concentration of the remaining fraction of PAEs in control experiments for direct photolysis (UV irradiation without photo-catalysts (Fe(III) or minerals) and with photo-catalyst (Fe(III) and minerals) but without irradiation (dark control).

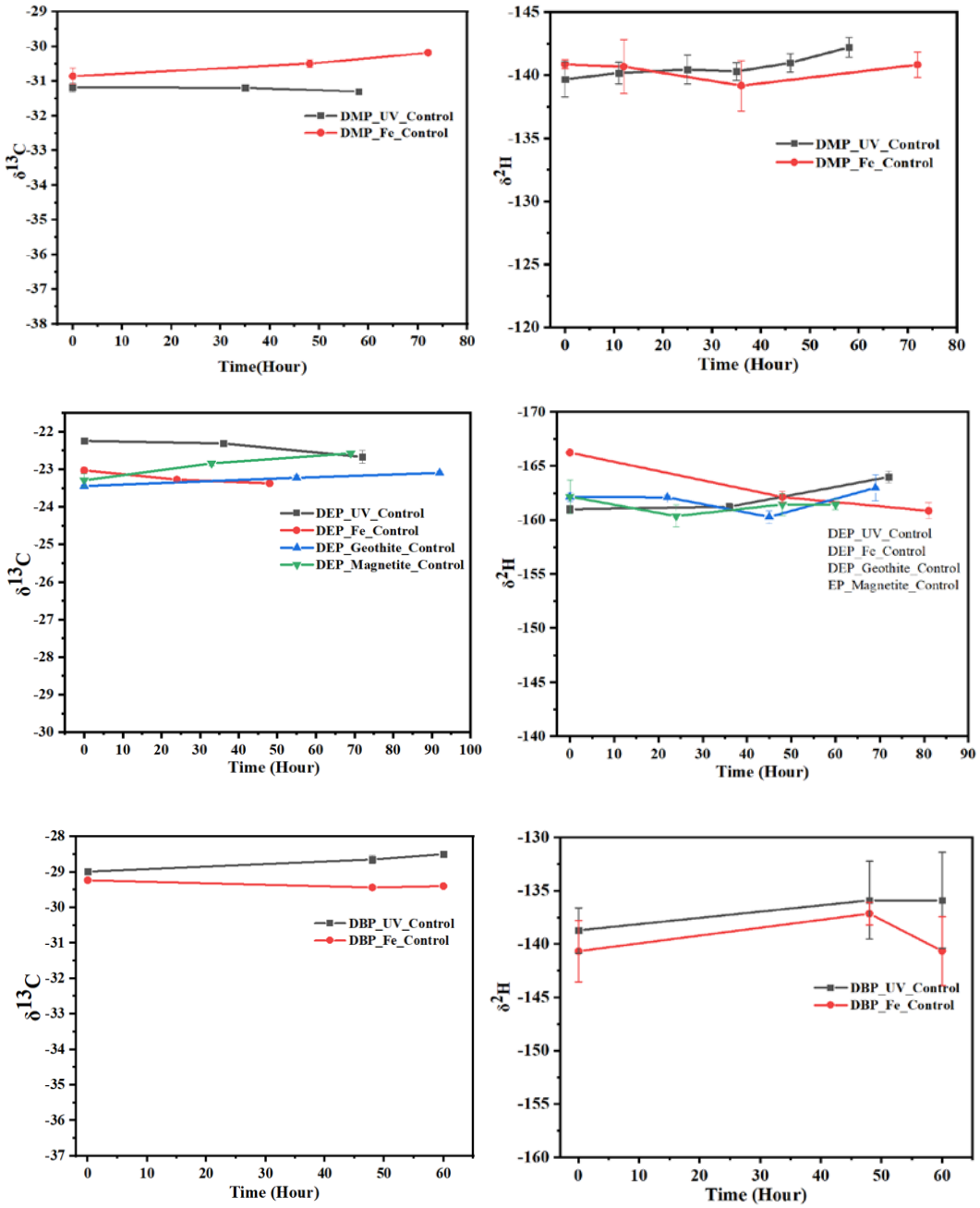


Figure S7. Carbon and hydrogen isotope composition the remaining fraction of PAEs in control experiments for direct photolysis (UV irradiation without photo-catalysts (Fe(III)aqua complex or iron minerals) and with photo-catalyst (Fe(III)aqua complex or iron minerals) but without irradiation (dark control).

4. Measurements of carbon and hydrogen isotope

All $\delta^{13}C$ and $\delta^{2}H$ values were normalized to the international standards of V-PDB (Vienna Pee Dee Belemnite) and VSMOW (Vienna Standard Mean Ocean Water), respectively (Grzegorz et al. 2022). The linearity range is shown in Fig. S8.

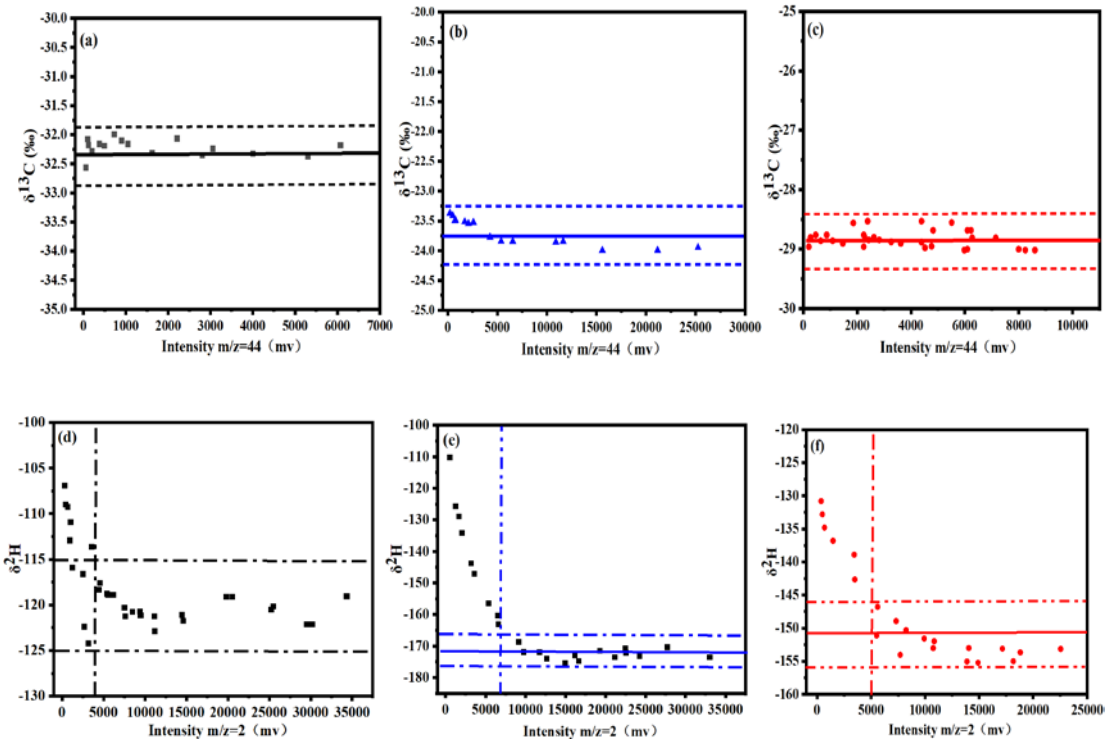


Figure S8. Isotope values of DMP, DEP and DBP versus the peak amplitude (mV), showing the linearity ranges for $\delta^{13}C$ (a for DMP, b for DEP and c for DBP) and $\delta^{2}H$ (d for DMP, e for DEP and f for DBP)

5. Degradation kinetics of PAEs in photochemical experiments with Fe(III) at different pH values and iron minerals

The degradation of PAEs (DMP, DEP and DBP) in all experiments can be described by a first order kinetic. The data are shown in Figure S9 and Figure S10.

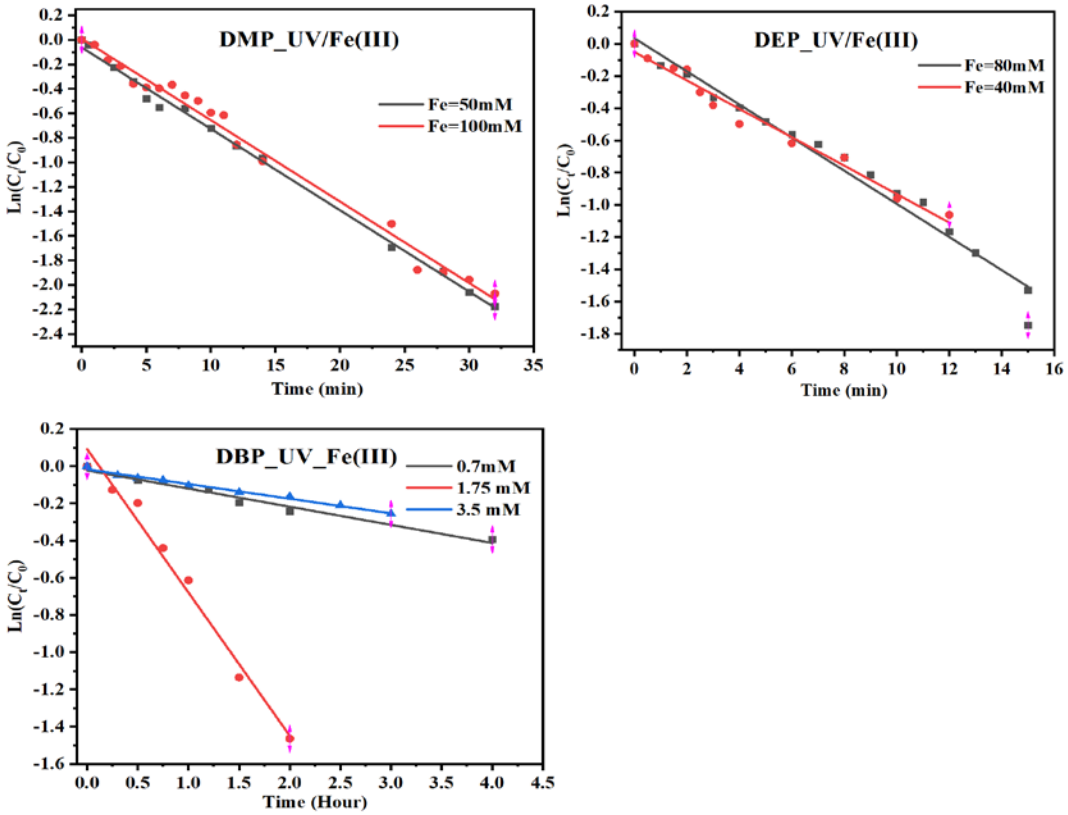


Figure S9. Effect of the Fe(III) concentration on PAEs degradation rate in UV/Fe(III)/PAEs experiments at pH 7. $[DMP]_0$ = 1.0 mM; $[DEP]_0$ = 0.8 mM; $[DBP]_0$ = 0.035 mM and $[Fe(III)]_0$ = 1.75, 3.5, 40, 50, 80, 100 mM.

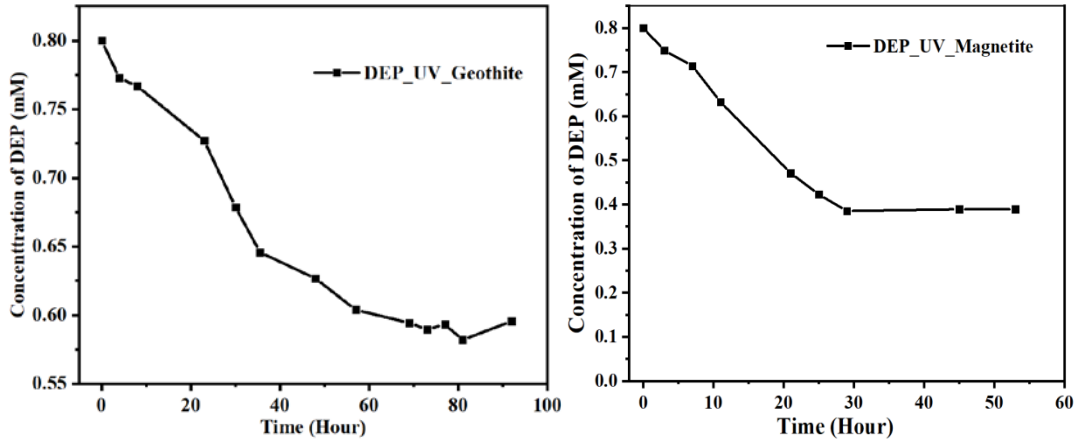


Figure S10. Effect of minerals (goethite and magnetite) on the degradation rate of DEP in UV/minerals experiments at pH = 7. $[DEP]_0$ = 0.8 mM; $[goethite]_0$ = 0.4 g L^{-1} and $[magnetite]_0$ = 0.4 g L^{-1}.

6. Quenching experiments with 2-propanol-D_8

In order to identify the predominant radical in the studied system, quenching experiments were conducted. The results show TBA inhibits the degradation of phthalates to a great extent, which indicates ·OH as the predominant radicals in the UV/Fe(III) system. In addition, experiments with 2-propanol-D_8 were conducted to confirm the presence of ·OH in the solution.

In the UV/Fe(III) experiment, 2-propanol-D_8 was rapidly oxidized by the ·OH resulting in the formation of acetone-D_6, which proves that ·OH play a major role in the systems (Figure S11). Acetone-D_6 was further degraded over the time course of the experiment. Acetone-D_6 was not detected in the experiment with goethite, which may indicate that ·OH is not an important radical formed in this solution (Figure S12(A)). We speculate that other radicals such as HO_2· may be the major radical in the experiment with UV and goethite. Small acetone-D_6 has been found in the system of UV/magnetite, which indicate ·OH and HO_2·may co-exist in this condition (Figure S12(B)).

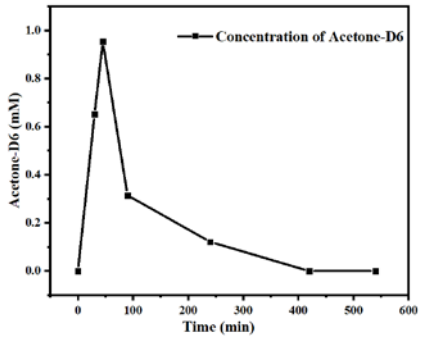


Figure S11. The concentration of acetone-D_6 in the system of UV/Fe(III).

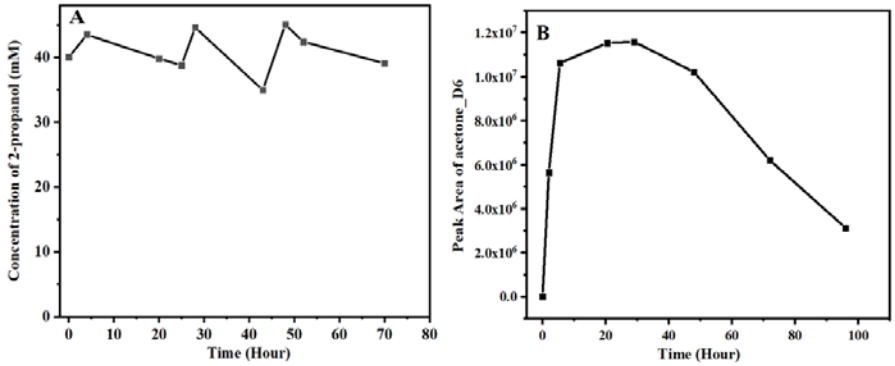


Figure S12. The concentration of 2-propanol-D_8 in the system of UV/goethite (A) and the concentration of acetone-D_6 in the system of UV/magnetite (B).

7. Identification of degradation products of PAEs formed during Fe(III)/UV experiments analyzed by GC-MS and FT-ICR MS

Transformation products were identified by GC-MS and FT-ICR MS in all experiments (Table S1). The methods are described in (Wu *et al.*, 2018).

Table S1: Identified intermediate photo transformation products.

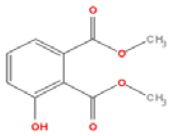
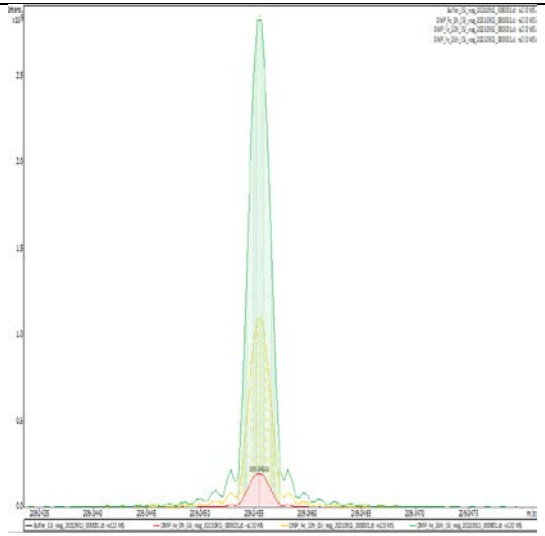
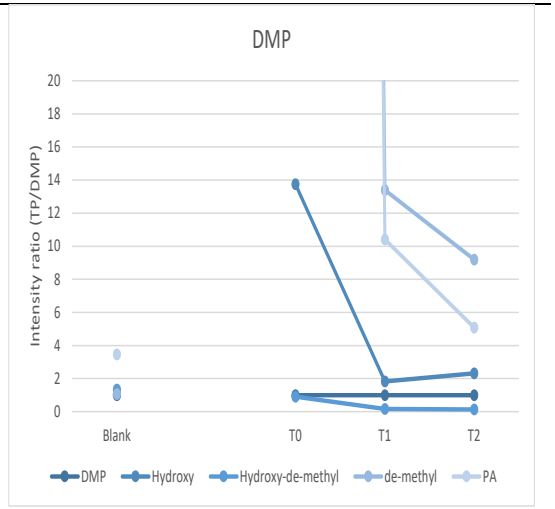
System	Structure	Molecular formula	GC-MS	(-)DI-FT-ICR MS (measured m/z)	
DMP UV/Fe(III)		$C_{10}H_{10}O_5$ 3-hydroxy-phthalic acid methyl ester	✓	209.405	 **Red for 0 h, Yellow for 13 h and Green for 26 h** 

Table S1 (cont'd): Identified intermediate phototransformation products

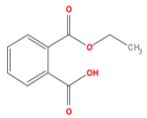
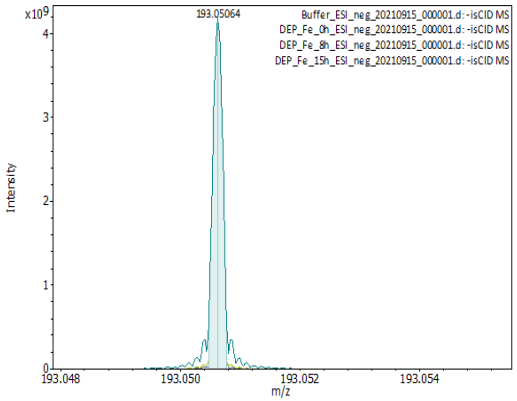
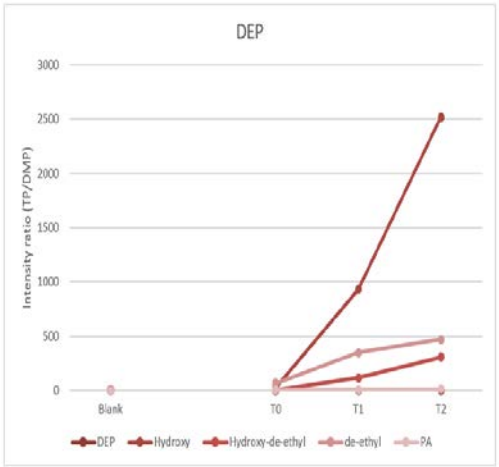
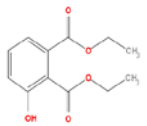
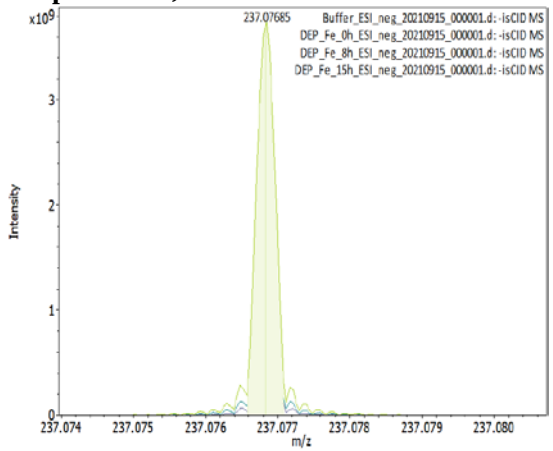
System	Structure	Molecular formula	GC-MS	(-)DI-FT-ICR MS(measured m/z)	
DEP UV/Fe(III)		$C_{10}H_{10}O_4$ phthalic acid ethyl ester	n.d.	193.0506	 **Purple for 0 h, Blue for 8 h and Green for 15h** 
		$C_{12}H_{14}O_5$ 3-hydroxy-phthalic acid diethyl ester	✓	237.0768	 **Purple for 0 h, Blue for 8h and Green for 15h**

Table S1 (cont'd): Identified intermediate phototransformation products

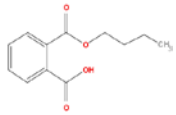
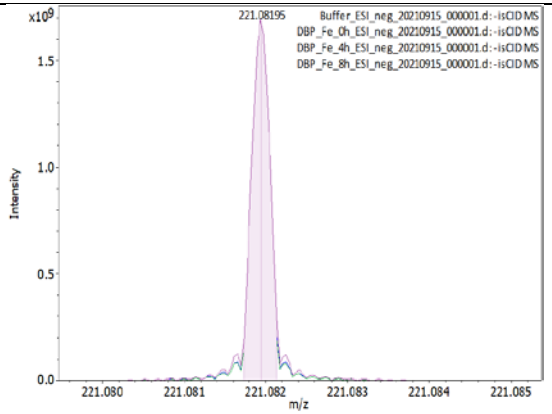
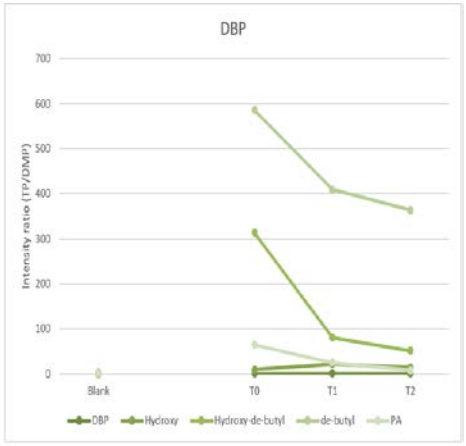
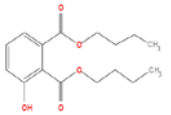
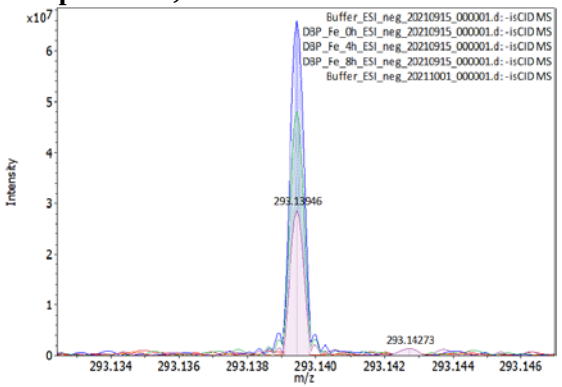
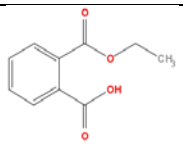
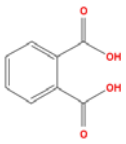
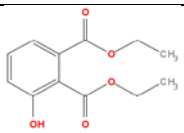
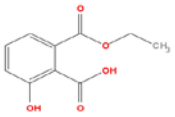
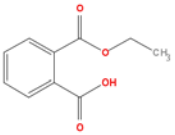
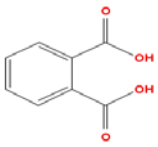
System	Structure	Molecular formula	GC-MS	(-)DI-FT-ICR MS(measured m/z)	
DBP UV/Fe(III)		$C_{12}H_{14}O_4$ phthalic acid butyl ester	n.d.	237.0768	 **Purple for 0h, Green for 4h and Blue for 15h** 
		$C_{16}H_{22}O_5$ 3-hydroxy-phthalic acid dibutyl ester	✓	293.1394	 **Red for 0h, Green for 4h and Purple for 15h**

Table S1 (cont'd): Identified intermediate photo-transformation products with tentative structures.

System	Structure	Molecular formula	GC-MS	(-)DI-FT-ICR MS (measured m/z)
DEP/UV/goethite		$C_{10}H_{10}O_4$ Phthalic acid ethyl ester	n.d.	193.05064
		$C_8H_6O_4$ Phthalic acid	n.d	165.01
DEP/UV/magnetite		$C_{12}H_{14}O_5$ 3-hydroxy-phthalic acid diethyl ester	✓	237.0768
		$C_{10}H_{10}O_5$ 3-Hydroxy- phthalic acid ethyl ester	n.d.	209.6455
		$C_{10}H_{10}O_4$ Phthalic acid ethyl ester	n.d.	193.05064
		$C_8H_6O_4$ Phthalic acid	n.d.	165.0193

8. Carbon and hydrogen isotope fractionation

The carbon and hydrogen isotope composition of DMP, DEP and DBP during the photocatalysis experiment with different concertation of Fe(III) are shown in Figure S13. In all UV/Fe(III) experiments, a normal stable carbon and hydrogen isotope effect (i.e. enrichment of the heavier isotopes in the remaining substrate) was observed (Figure S13). In contrast, a normal carbon and inverse hydrogen isotope fractionation has been observed in experiments with Fe-minerals and UV irradiation (>280 nm) (Figure S14).

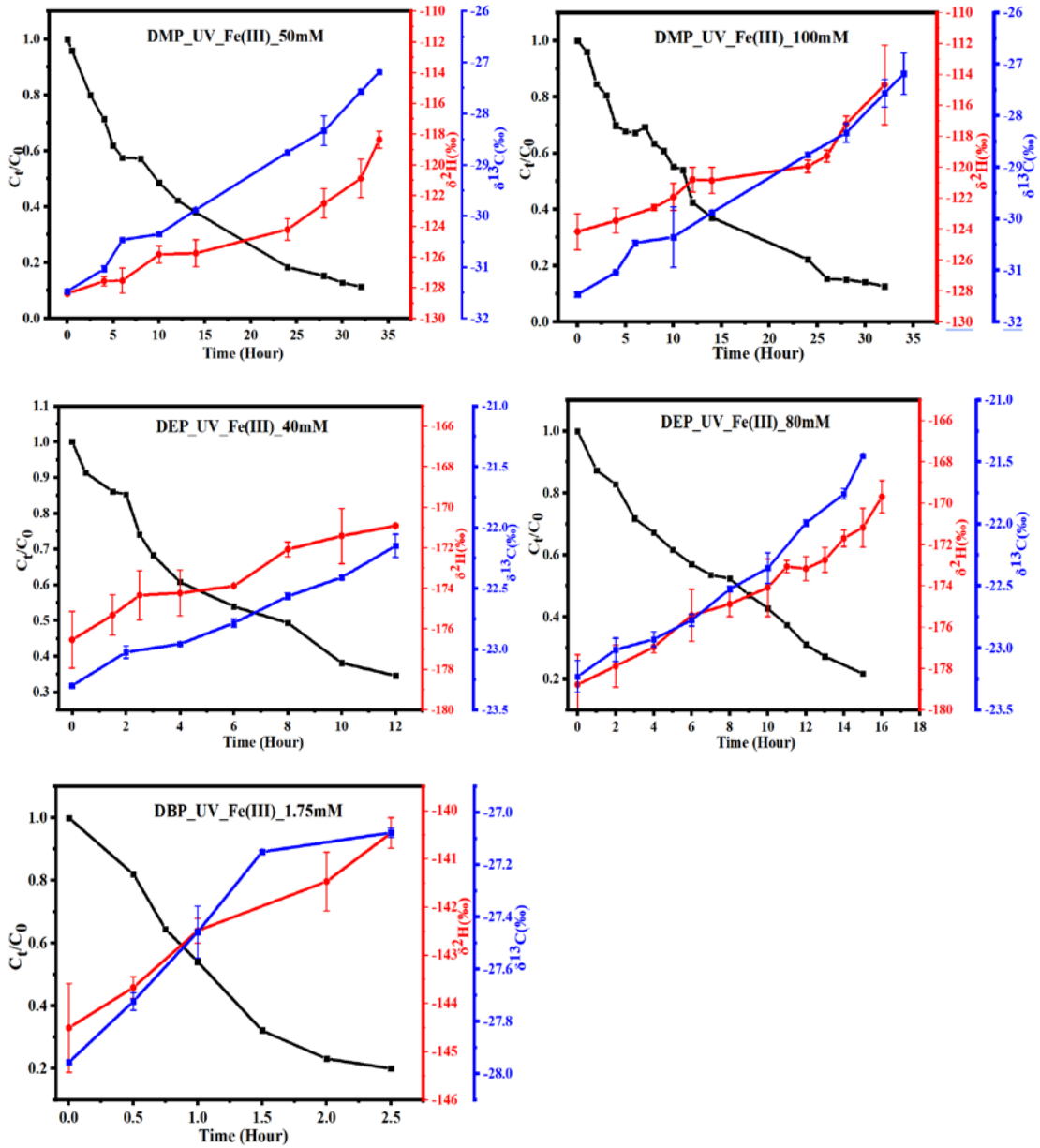


Figure S13. Carbon and hydrogen isotopic composition of PAEs during the photocatalysis experiment with Fe(III).

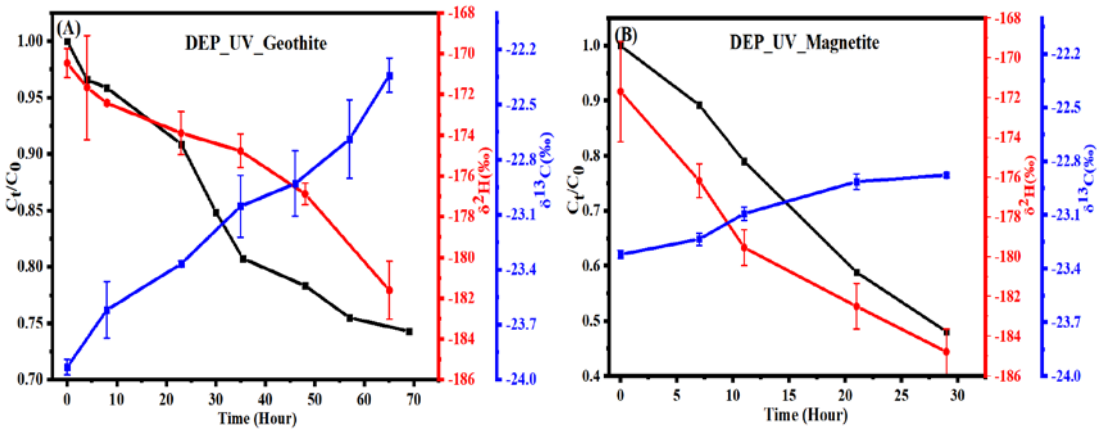


Figure S14. Carbon and hydrogen isotopic composition of PAEs during the photocatalysis experiment with goethite (A) magnetite (B).

9. The apparent kinetic isotope effect (AKIE) calculation

Apparent kinetic isotope effects (AKIEs) were calculated based on the determined isotopic fractionation according to Eq. (15) for correcting for the isotope dilution effect by non-reactive atoms and the intramolecular competition in DMP, DEP and DBP molecules. During the hydrolysis reactions of esters, the cleavage of the should carbonyl group to form an acid and an alcohol should result in a primary $AKIE_C$. For DMP ($C_{10}H_{12}O_4$), $AKIE_C$ was calculated using n = 12, x = 2 and z = 2, because C-O bonds in two ester groups compete for the reaction. Similarly, the values of x and z were both 4 and 4 for DEP ($C_{12}H_{14}O_4$) and DBP ($C_{14}H_{16}O_4$), while n were 12 and 16, respectively. In the hydrolysis reaction $AKIE_H$ of phthalates is a considered to be associated with a secondary isotope effect as H is not directly involved in a bond change reaction. The calculation may by simplified to x = 4 and z = 4 as the only the C-H bond may affect the C-O bond cleavage as directly attached to the reactive carbons.

For calculation of ^{13}C-AKIE during UV/H_2O_2 reaction we assume a preferential of •OH radicals with the aromatic ring according to the RAF pathway. For DMP ($C_{10}H_{10}O_4$) n, x and z are 10, 2 and 2, respectively. For DEP ($C_{12}H_{14}O_4$) n, x and z are 12, 2 and 2, respectively. For DBP ($C_{14}H_{16}O_4$) n, x and z are 14, 2 and 2, respectively. Similarly, the apparent kinetic isotope effect ^{2}H-AKIE for the RAH pathway were calculated (DMP n = 10, x = 2, z = 2; DEP n = 14, x = 2, z = 2, DBP n = 16, x = 2, z = 2).

Similarly, we calculate the ^{13}C-AKIE and ^{2}H-AKIE of the Fe(III) catalyzed reaction assuming that •OH were dominant and indeed the AKIEs were similar to the photosynthesized reaction with H_2O_2.

The apparent kinetic isotope effect (^{2}H-AKIE, ^{13}C-AKIE) of DEP and DBP during the and UV/Fe-mineral reaction (goethite and magnetite) were calculated assuming a preferential reaction at the aromatic ring and compared to AKIE values found in the literature and in the photoinduced reaction with Fe(III) and H_2O_2 both forming preferentially •OH. The AKIEs of the UV/Fe-mineral reactions are completely different leading to the hypothesis that the mechanism with solid surfaces may have a different mechanism and •OH do not play a role.

Reference

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