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## Exploring the effects of pulsed ultrasound at 205 and 616 kHz on the sonochemical degradation of octylbenzene sulfonate

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### ABSTRACT

Compared to continuous wave (CW) ultrasound, pulsed wave (PW) ultrasound has been shown to result in enhanced sonochemical degradation of octylbenzene sulfonate (OBS). However, pulsed ultrasound was investigated under limited pulsing conditions. In this study, pulse-enhanced degradation of OBS was investigated over a broad range of pulsing conditions and at two ultrasonic frequencies (616 and 205 kHz). The rate of OBS degradation was compared to the rate of formation of 2-hydroxyterephthalic acid (HTA) following sonolysis of aqueous terephthalic acid (TA) solutions. This study shows that sonication mode and ultrasound frequency affect both OBS degradation and HTA formation rates, but not necessarily in the same way. Unlike TA, OBS, being a surface active solute, alters the cavitation bubble field by adsorbing to the gas/solution interface of cavitation bubbles. Enhanced OBS degradation rates during pulsing are attributed to this adsorption process. However, negative or smaller pulse enhancements compared to enhanced HTA formation rates are attributed to a decrease in the high-energy stable bubble population and a corresponding increase in the transient bubble population. Therefore, sonochemical activity as determined from TA sonolysis cannot be used as a measure of the effect of pulsing on the rate of degradation of surfactants in water. Over relatively long sonolysis times, a decrease in the rate of OBS degradation was observed under CW, but not under PW conditions. We propose that the generation and accumulation of surface active and volatile byproducts on the surface and inside of cavitation bubbles, respectively, during CW sonolysis is a contributing factor to this effect. This result suggests that there are practical applications to the use of pulsed ultrasound as a method to degrade surface active contaminants in water.

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### 1. Introduction

High power ultrasound has been proposed as a potential advanced oxidation technology to degrade linear alkyl benzene sulfonates (LAS) [1] and other surface active compounds in water [2] such as alkyl ethoxylates (APEs) [3,4] and perfluorinated surfactants such as perfluorooctane sulfonate (PFOS) [5] and perfluorooctanoic acid (PFOA) [6,7]. One of the major limitations in using ultrasound as an advanced oxidation process is the low efficiency to cost ratio [8]. We have shown that efficiency is improved, in some cases considerably, by pulsing the ultrasonic wave [9–11].

When ultrasound is passed through a liquid, cavitation occurs, i.e., the formation and rapid collapse of gas/vapor filled microbubbles. The collapse of cavitation bubbles is almost adiabatic in nature, resulting in the formation of hot spots, nano-sized regions of extremely high temperatures and pressures [12,13]. Three

possible reaction zones where contaminants decompose exist: (1) The interior of the bubble where volatile contaminants undergo thermolysis. (2) A hot-liquid shell surrounding the hot spot where thermolysis and radical abstraction reactions occur between surface active contaminants and H and OH radicals formed by thermolysis of water vapor inside collapsing bubbles. (3) The bulk solution where radical reactions and reactions with reactive by-products, such as hydrogen peroxide occur. Since LAS is non-volatile and surface active, the majority of its sonochemical decomposition is expected to occur through thermolysis and radical reactions at the gas/solution interface of the cavitation bubbles, which is common to the sonolysis of aqueous surfactant solutions [14,15].

It has been shown that adsorption of surfactants to the gas/solution interface of cavitation bubbles depends on the thermodynamic [16–19] and the kinetic/diffusion-controlled adsorption properties of these solutes [14,20,21]. In an attempt to enhance the ultrasound-induced degradation efficiency of surface active contaminants in water, we have investigated the use of pulsed ultrasound exposure [9–11,22]. These studies show that pulsed ultrasound results in the enhancement of the sonochemical

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degradation of surface active contaminants in aqueous solutions, since the lifetime of the gas/solution interface and/or the bubble lifetime increases during the pulse intervals. This may enhance kinetically-driven adsorption of surfactants to the short-lived gas/solution interface of cavitation bubbles during the pulse interval, where decomposition of the surfactant occurs during the ensuing ultrasound pulse. In addition to enhancing kinetically-driven adsorption, the ability of ultrasound to produce chemically active bubbles in a given solution will depend on the ratio of the ultrasonic pulse length ( $T$ ) to pulse interval ( $T_0$ ) [9,23–27].

Yang et al. [11] found that the sonochemical degradation of surfactants was not uniformly enhanced during pulsing and strongly depended on the  $T$  and  $T_0$  times. Furthermore, enhancement in the degradation rate of surfactants during pulsed ultrasound depended on the frequency of ultrasound. However, pulse enhancement was investigated under a fairly limited range of pulsing conditions. In order to gain a clearer understanding of this effect, the current study investigated the sonochemical degradation of octylbenzene sulfonate (OBS, as a model compound representative of surface active contaminants) under a wide range of ultrasound pulsing conditions at 205 and 616 kHz. Additionally, these results are compared to the OH radical formation rate in the absence of OBS and under identical conditions of sonolysis, as a measure of the sonochemical yield in the solution.

## 2. Methods

### 2.1. Chemicals

The sodium salt of 4-octyl benzenesulfonate (OBS; 97%) was obtained from Sigma–Aldrich Corp. Terephthalic acid (TA; 99 + %) was obtained from Acros Chemicals. Potassium phosphate monobasic (certified ACS), sodium phosphate dibasic anhydrous (certified ACS), sodium hydroxide (NF/FCC) acetonitrile (HPLC Grade), sodium phosphate monobasic anhydrous (certified ACS) and o-phosphoric acid were obtained from Fisher Scientific. Purified Milli-Q filtered water ( $R = 18.2 \text{ M}\Omega\text{-cm}$ ) was used in all experiments.

### 2.2. Ultrasound apparatus

Flat plate transducers (Models: USW 51-106 and USW 51-051) operating at a frequency of 69, 205, or 616 kHz (ELAC-Nautik, L-3 Communication, GmbH, Kiel, Germany) emitted ultrasound through a round stainless steel plate ( $A = 23.4 \text{ cm}^2$ ). A custom cylindrical glass reactor ( $V = 320 \text{ mL}$ ), was open at the bottom and clamped to the top of the housing of a flat plate transducer. This reactor also had two ports at the top for obtaining samples. The glass reactor was surrounded by an outer water jacket that was attached to a water cooling system (Isotemp 1006S, Fisher Scientific) to maintain the solution at  $20 \pm 1^\circ\text{C}$ . Solution (300 mL) was poured into the glass ultrasonic reactor and exposed to ultrasound while in direct contact with the stainless steel flat plate. After each experiment the reactor was rinsed three times with Milli-Q water. To improve reproducibility, the reactor was never separated from the transducer housing between experiments under the same frequency [28].

### 2.3. Ultrasound exposure

Power was supplied to the ultrasonic transducer through a function/pulse generator (SM-1020; Signametrics Corp., Seattle, WA) and magnified by a linear amplifier (AG 1021; T&C Power Conversion, Inc., Rochester, NY). Continuous and pulsed electrical signals of 30, 60, 100, 160 and 320 ms for  $T$  and  $T_0$  were generated

for the experiments. Twenty-five different pulse combinations (i.e.  $T$  and  $T_0$ ) were studied at each ultrasonic frequency. Comparisons between continuous and pulsed experiments were made at a constant sonication time. An oscilloscope (model: 54501, 100 MHz Digitizing Oscilloscope, Hewlett Packard) was used to verify the wave properties of the pulse experiments. Frequency tuning, impedance tests and pressure tests were conducted on all transducers to check the functionality before beginning this research. All temperature measurements were performed using a thermocouple (Omega Corporation, Stamford, CT), which was connected to a Fluke industrial scope meter (model 123, supplied by Everett, WA).

The power input into a 300 mL solution for both continuous and pulsed ultrasonic modes was  $27 \pm 1.5 \text{ W}$ , as measured by calorimetry [29,30]. This power was chosen for all experiments, because it is within a linear range between ultrasound intensity and sonochemical yield at 69, 205, and 616 kHz.

To have a comparable ultrasonic irradiation time during all experimental sets, the following equation was used to calculate the total experimental time [24]:

$$t_{\text{experimental}} = t_{\text{sonolysis}} \left( 1 + \frac{T_0}{T} \right) \quad (1)$$

where,  $t_{\text{experimental}}$  is the total time of the experiment,  $t_{\text{sonolysis}}$  is the total time that the system is irradiated by ultrasound during an experiment,  $T_0$  is the silent time during one pulse cycle, and  $T$  is the irradiation time during one pulse cycle.

### 2.4. Analysis

**OBS:** To avoid any potential complications due to the formation of micelles [3,14,31,32] all experiments in the current study were conducted at an initial OBS concentration of 1 mM. The surface tension of aqueous OBS solutions (0–15 mM) was measured by the expanding bubble technique [33] with a Sensadyne surface tensiometer, (Model PC 500, Chem-Dyne Research Corp., Mesa, AZ) confirming that 1 mM was well below the critical micelle concentration (CMC) of OBS.

Samples (200  $\mu\text{L}$ ) for OBS analysis were collected a total of 11 times over the course of an ultrasound experiment. The samples were stored under refrigeration in 2 mL glass HPLC vials (Agilent Technologies, New Castle, DE), for a maximum of three days prior to HPLC analysis. In control experiments, storage was determined to have no effect on the OBS concentration following sonolysis.

A HPLC (Hewlett Packard, model 1100) with a  $100 \times 2.1 \text{ mm}$  C18 ODS Hypersil column (Thermo Electron Corp., Bellefonte, PA) and eluent of 33% acetonitrile and 67% phosphate buffer ( $\text{pH} = 2.2$ ) was used to determine the OBS concentration following sonolysis of aqueous OBS solutions.

**HTA:** Hydroxyl radical formation during sonolysis was determined by sonicating buffered TA solutions (1 mM; 300 mL). TA combines with the generated OH radicals in a 1:1 M ratio to form hydroxyterephthalate (HTA), which has fluorescent properties. This fluorescent yield was detected over the length of each experiment (6 samples; 3 mL ea.) using a Shimadzu RF-5301 PC spectrofluorophotometer (Columbia, MD). These samples were delivered into a quartz cell with a 10 mm-path-length for insertion into the spectrofluorophotometer. The following parameters were used in this analysis: excitation and emission beam slit width 1.5 nm, sampling interval 0.2 nm, excitation wavelength 315 nm, and an optimal emission wavelength was determined to be 428 nm. For calibration purposes, HTA was synthesized according to Field and Engelhardt [34].

**DATA ANALYSIS:** Experiments were typically run in duplicate unless stated otherwise. Upon analysis of the data set by the SAS

statistical program, JMP, linear regression analysis through blocking by experiment was used as a technique to attempt to alleviate nuisance variables [35]. Briefly, this technique weights the correlation values of each data point from the duplicate or triplicate experiments and calculates a single slope, alternate to just averaging the slopes of each regression line. The calculated slope better represents the true rate constant and reported standard error.

### 3. Results

Fig. 1 shows ultrasound-mediated (616 kHz) degradation of OBS (1 mM, 300 mL) under continuous wave (CW) and pulsed wave (PW) exposure with  $T = 100$  ms and  $T_0 = 100$  ms. All degradation data fit to apparent pseudo first-order kinetics. The rate constant of degradation was constant for only the first 20 min of CW sonolysis ( $k = 5.7 \times 10^{-3} \text{ min}^{-1}$ ), after which time an inflection point in the rate constant of degradation occurs, resulting in a decrease of the rate constant to  $k = 3.0 \times 10^{-3} \text{ min}^{-1}$ . A similar phenomenon has been observed previously in solutions of surface active compounds [1,36]. Interestingly, this inflection point in the rate of OBS degradation was not observed when the ultrasound wave was pulsed for up to 60 min. of sonolysis ( $k = 5.1 \times 10^{-3} \text{ min}^{-1}$ ), (Fig. 1).

A similar result (Fig. 2) was observed at a frequency of 205 kHz with an initial degradation rate constant under continuous wave ultrasound of  $k = 5.5 \times 10^{-3} \text{ min}^{-1}$  that decreased at times greater than 15 min ( $k = 2.1 \times 10^{-3} \text{ min}^{-1}$ ). Similar to findings at 616 kHz (Fig. 1) PW ultrasound maintained uniform first-order kinetics over the entire experiment. In separate experiments at sonolysis times of up to 15 min, the initial OBS degradation rate was confirmed to be constant at both frequencies and have a linear dependence on sonolysis time under both CW and PW exposure conditions (e.g., Fig. 3). Therefore, to compare the effect of PW and CW modes on the sonochemical rate of degradation of OBS, all comparisons were made at 15 min sonolysis time. Tables 1 and 2, show the weighted OBS degradation rate constants with standard errors, determined for CW and PW settings at 616 and 205 kHz,

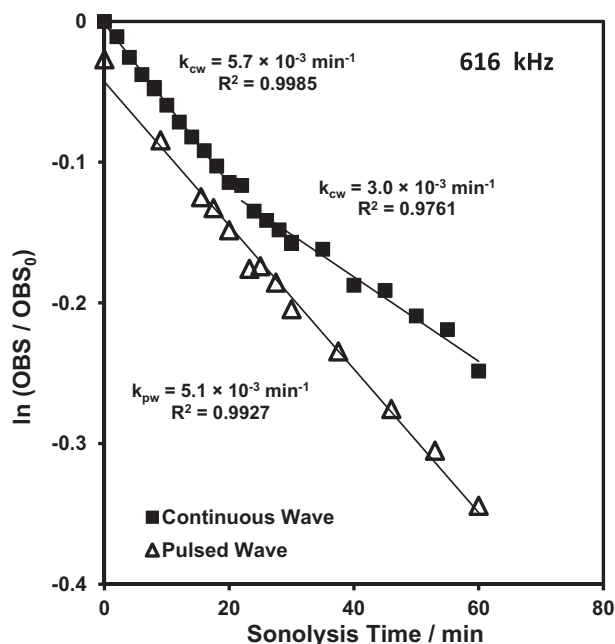


Fig. 1. Degradation of aqueous OBS (1 mM, 300 mL) solution exposed to continuous and pulsed wave ( $T = 100$  ms;  $T_0 = 100$  ms) ultrasound ( $f = 616$  kHz;  $P = 27$  W;  $T = 20$  °C).

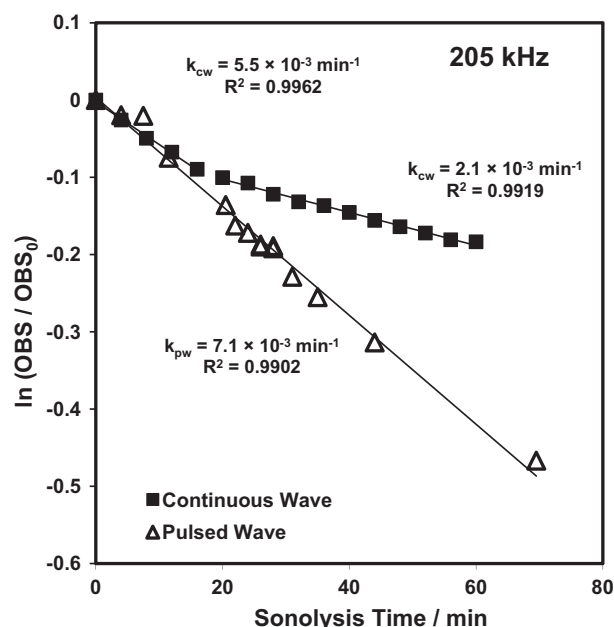


Fig. 2. Degradation of aqueous OBS (1 mM, 300 mL) solution exposed to continuous and pulsed wave ( $T = 100$  ms;  $T_0 = 100$  ms) ultrasound ( $f = 205$  kHz;  $P = 27$  W;  $T = 20$  °C).

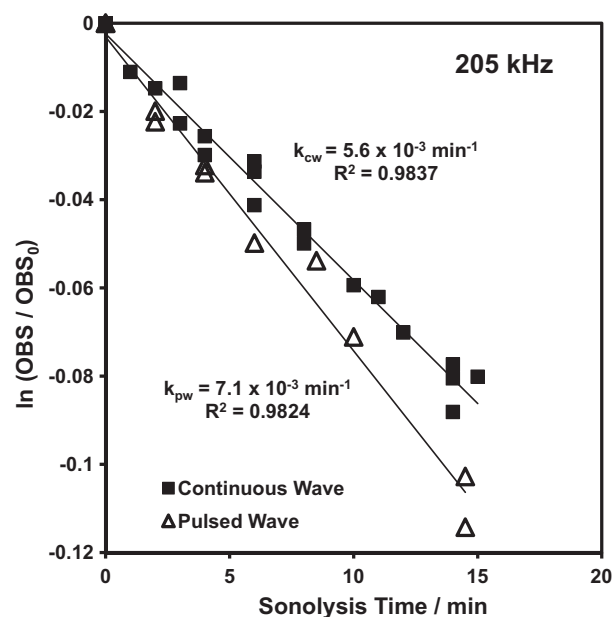


Fig. 3. First order degradation plot of aqueous OBS (run in triplicate), (1 mM, 300 mL) solution exposed to continuous and pulsed wave ( $T = 100$  ms;  $T_0 = 100$  ms) ultrasound ( $f = 205$  kHz;  $P = 27$  W;  $T = 20$  °C).

respectively. It is clear from the data in these tables that the results are highly reproducible.

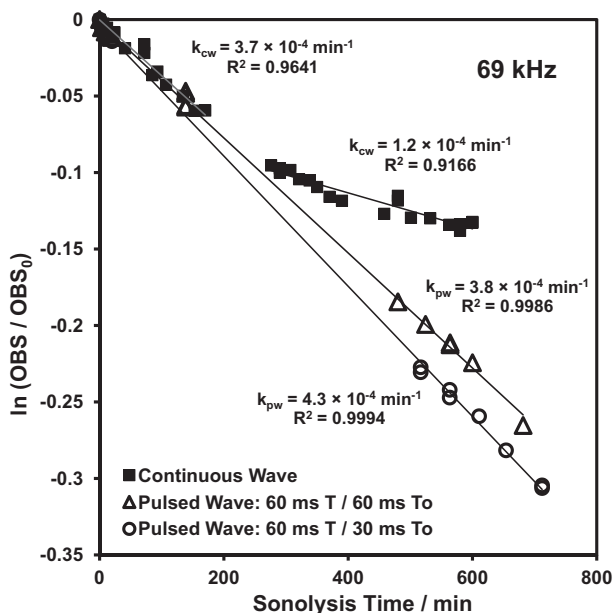
In practice, relatively low frequency ultrasound is typically used for industrial scale processing applications [2,37,38]. For this reason, the effect of PW mode on the degradation of OBS at 69 kHz was investigated, as shown in Fig. 4. Similar, to the results shown at 616 and 205 kHz, an inflection point exists in the rate of degradation of OBS at 69 kHz CW sonolysis at an exposure time of 150 min, where the rate constant of degradation changes from  $k = 3.7 \times 10^{-4} \text{ min}^{-1}$  to  $k = 1.4 \times 10^{-4} \text{ min}^{-1}$ . Under all frequencies investigated, this inflection point occurs at a similar

**Table 1**  
616 kHz OBS and HTA  $k_{\text{weighted}}$  values and associated standard errors are shown at each pulsed setting. These values were calculated using the SAS statistical program JMP.

Continuous	Pulsing	Pulse interval/ms				
	Pulse length/ms	30	60	100	160	320
<i>Initial OBS degradation rate constant <math>\{k \pm \text{std error (min}^{-1})\} \times 10^3</math></i>						
$5.7 \pm 0.05$	30	$6.2 \pm 0.2$	$5.5 \pm 0.3$	$5.4 \pm 0.2$	$4.8 \pm 0.3$	$3.3 \pm 0.3$
	60	$5.8 \pm 0.2$	$5.6 \pm 0.3$	$5.5 \pm 0.1$	$5.7 \pm 0.3$	$6.8 \pm 0.1$
	100	$5.8 \pm 0.1$	$5.5 \pm 0.1$	$6.3 \pm 0.1$	$5.7 \pm 0.3$	$5.0 \pm 0.2$
	160	$5.8 \pm 0.1$	$5.6 \pm 0.2$	$5.7 \pm 0.1$	$5.9 \pm 0.1$	$5.8 \pm 0.3$
	320	$5.3 \pm 0.1$	$5.7 \pm 0.1$	$5.6 \pm 0.1$	$5.2 \pm 0.2$	$5.7 \pm 0.1$
<i>Initial HTA formation rate constant <math>\{k \pm \text{std error (mM min}^{-1})\} \times 10^3</math></i>						
$0.695 \pm 0.007$	30	$0.823 \pm 0.004$	$0.803 \pm 0.005$	$0.776 \pm 0.004$	$0.747 \pm 0.006$	$0.729 \pm 0.004$
	60	$0.780 \pm 0.007$	$0.783 \pm 0.007$	$0.770 \pm 0.005$	$0.762 \pm 0.008$	$0.726 \pm 0.010$
	100	$0.786 \pm 0.008$	$0.790 \pm 0.007$	$0.759 \pm 0.006$	$0.765 \pm 0.006$	$0.722 \pm 0.007$
	160	$0.779 \pm 0.007$	$0.774 \pm 0.005$	$0.776 \pm 0.008$	$0.767 \pm 0.009$	$0.762 \pm 0.007$
	320	$0.781 \pm 0.007$	$0.780 \pm 0.007$	$0.794 \pm 0.009$	$0.781 \pm 0.007$	$0.770 \pm 0.006$

**Table 2**  
205 kHz OBS and HTA  $k_{\text{weighted}}$  values and associated standard errors are shown at each pulsed setting. These values were calculated using the SAS statistical program JMP.

Continuous	Pulsing	Pulse interval/ms				
	Pulse length/ms	30	60	100	160	320
<i>Initial OBS degradation rate constant <math>\{k \pm \text{std error (min}^{-1})\} \times 10^3</math></i>						
$5.3 \pm 0.11$	30	$5.3 \pm 0.1$	$6.2 \pm 0.2$	$5.8 \pm 0.4$	$6.1 \pm 0.1$	$4.7 \pm 0.8$
	60	$6.0 \pm 0.1$	$4.8 \pm 0.2$	$5.6 \pm 0.2$	$6.5 \pm 0.3$	$6.5 \pm 0.2$
	100	$6.1 \pm 0.2$	$5.5 \pm 0.2$	$7.2 \pm 0.3$	$5.4 \pm 0.3$	$5.9 \pm 0.1$
	160	$5.9 \pm 0.2$	$5.5 \pm 0.1$	$5.2 \pm 0.2$	$5.7 \pm 0.1$	$6.3 \pm 0.3$
	320	$5.3 \pm 0.3$	$5.8 \pm 0.3$	$5.7 \pm 0.1$	$5.2 \pm 0.1$	$4.7 \pm 0.2$
<i>Initial HTA formation rate constant <math>\{k \pm \text{std error (mM min}^{-1})\} \times 10^3</math></i>						
$0.713 \pm 0.005$	30	$0.708 \pm 0.008$	$0.726 \pm 0.007$	$0.746 \pm 0.008$	$0.712 \pm 0.008$	$0.759 \pm 0.007$
	60	$0.737 \pm 0.008$	$0.722 \pm 0.003$	$0.672 \pm 0.007$	$0.735 \pm 0.009$	$0.695 \pm 0.004$
	100	$0.711 \pm 0.004$	$0.699 \pm 0.005$	$0.686 \pm 0.005$	$0.711 \pm 0.008$	$0.68 \pm 0.02$
	160	$0.71 \pm 0.02$	$0.655 \pm 0.005$	$0.697 \pm 0.004$	$0.720 \pm 0.006$	$0.704 \pm 0.006$
	320	$0.722 \pm 0.003$	$0.701 \pm 0.004$	$0.677 \pm 0.004$	$0.695 \pm 0.008$	$0.710 \pm 0.005$



**Fig. 4.** Degradation of aqueous OBS (1 mM, 300 mL) exposed to continuous and pulsed wave ( $T = 60$  ms;  $T_0 = 60$  or 30 ms) ultrasound ( $f = 69$  kHz;  $P = 27$  W;  $T = 20$  °C).

again follows a linear trend under first-order kinetic conditions throughout the experiment.

To gain an understanding of the effect of PW ultrasound on the sonochemical rate of OBS degradation at 616 and 205 kHz, the apparent rate of OH formation in the bulk solution using TA solutions under CW and PW sonolysis conditions was measured. The sonochemical rate of formation of HTA was performed at  $[TA]_{\text{initial}} = 1$  mM, which was empirically determined [39] to ensure an excess amount of TA in the solution during the experiment [40,41]. In earlier studies on the sonochemical rate of formation of HTA from aqueous TA solutions, Fang et al. [42], observed that the rate of HTA formation remained constant below an empirically determined sonolysis time, after which time the formation rate decreased due to the sonochemical degradation of HTA [42]. Therefore, the rate of formation of HTA in the current study was only determined at sonolysis times of up to 10 min, to ensure a linear dependence on sonolysis time [39].

Fig. 5 shows the concentration of HTA formed during exposure of aqueous TA solutions under CW and PW ultrasound, at 205 kHz. The sonochemical rate of formation of HTA follows zero-order kinetics as shown in Tables 1 and 2 under all CW and PW conditions investigated at 616 and 205 kHz, respectively. Also shown are the first-order degradation rate constants of OBS.

Tables 1 and 2 show that the first-order rate constants for OBS degradation and the zero order formation rate constants of HTA depend on the PW condition, within a given ultrasound frequency. From the complete data sets at 205 and 616 kHz, it is possible to gain an understanding of how pulsing the ultrasound wave affects the sonochemical degradation of OBS at different ultrasound frequencies, compared to the total sonochemical activity in a system, determined from the sonochemical formation rate of HTA.

OBS degradation percentage (i.e., 7–10%). Consistent with the results observed following sonolysis at 616 and 205 kHz, sonochemical degradation of OBS under PW conditions at 69 kHz



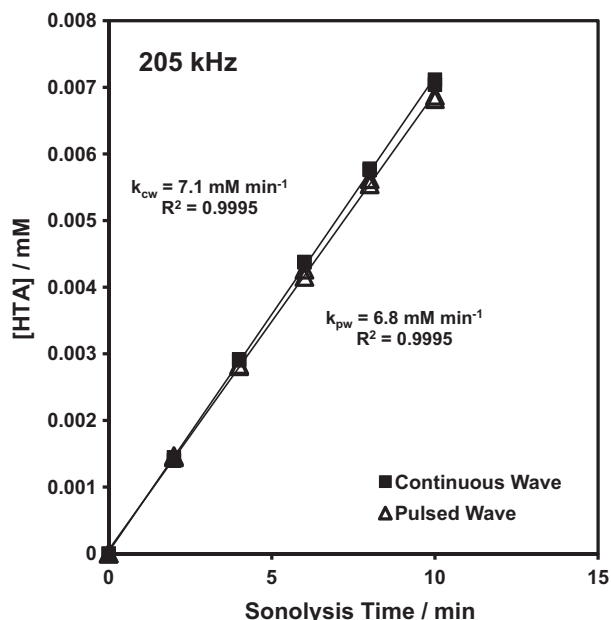


Fig. 5. Formation of aqueous HTA (run in duplicate) (TA = 1 mM, 300 mL) solutions exposed to continuous and pulsed wave ( $T = 100$  ms;  $T_0 = 100$  ms) ultrasound ( $f = 205$  kHz;  $P = 27$  W;  $T = 20$  °C).

#### 4. Discussion

Tables 1 and 2 show a variety of PW conditions resulting in statistically significant changes in both the rate constant of degradation of OBS and the rate constant of HTA formation compared to that observed during CW exposure. As described by Yang et al. [11] the rate of HTA formation depends on the number of  $\cdot\text{OH}$  that react with TA in bulk solution, which depends on the number of inertial cavitation bubbles, the final bubble temperature, the partial pressure of water vapor inside of the bubble just prior to collapse and the number of  $\cdot\text{OH}$  that escape to the bulk. These parameters depend on the frequency and mode of sonication and consequently affect the rate of OBS degradation. In addition to this, adsorption of OBS to the gas/solution interface also plays a role in the rate of thermolysis of adsorbed surfactant [14] and on coalescence [43], declustering [19] and the thermodynamic stability of bubbles (namely through Laplace pressure effects) [20].

In sonochemistry, it is not possible to make quantitative measurements on the effect of ultrasound frequency on sonochemical rates, since there is no known measure for the energy conversion efficacy of cavitation bubbles when the US frequency is changed. For this reason, the comparative method in sonochemistry was developed [20,44,45]. The main assumption of the comparative method is that the cavitation bubble field is constant when comparisons of the sonochemical rate of two reactions are made under a given set of ultrasound exposure conditions. However, this assumption is not entirely true in the current study, due to the possible effects of OBS on the bubble population (as described above) which also need to be considered when making comparisons with HTA formation rates as a measure of the sonochemical activity in the system.

To compare pulsed ultrasound rates to continuous ultrasound exposure rates for each experiment and at 616 and 205 kHz the “pulse enhancement”, (PE) was calculated which is a measure of the effect of pulsing on the rate of reaction, as shown in Eq. (2) [9–11]:

$$\text{Pulse Enhancement}(\%) = \frac{k_{pw} - k_{cw}}{k_{cw}} \times 100 \quad (2)$$

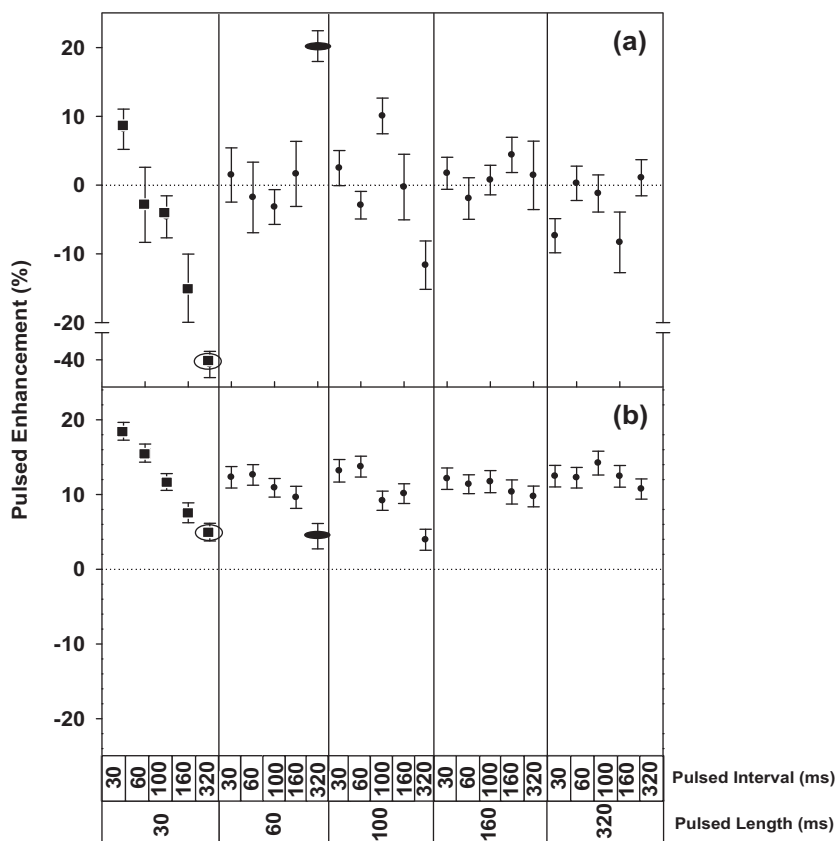
where  $k$  is the degradation rate constant for OBS or formation rate constant for HTA;  $k_{pw}$  is the sonochemical rate constant observed under PW sonolysis and  $k_{cw}$  is observed during CW ultrasound exposure. Using Eq. (2), a positive PE value indicates a faster rate of reaction during PW exposure than during CW exposure, and vice versa. PE values are shown in Figs. 6 and 7 for 616 kHz and 205 kHz ultrasound exposure, respectively. Continuous wave experiments are represented by a dashed line at PE = 0%. Surprisingly, PE values did not follow any consistent trends with PW conditions for either OBS or HTA. However,  $T = T_0 = 100$  ms studied previously [11] did yield positive PE values under both frequencies.

In order to understand the seemingly complicated results shown in Figs. 6 and 7, data in Figs. 6 and 7 were used to compare the PE for OBS degradation to that of HTA formation (i.e.,  $\text{PE}_{(\text{OBS})}$ :  $\text{PE}_{(\text{HTA})}$ ) at a given frequency and pulsed mode. A finite number of combinations of  $\text{PE}_{(\text{OBS})}$ : $\text{PE}_{(\text{HTA})}$  are possible, and are grouped into sets of similar data, as shown in Table 3. Set 1 contains all of the combinations where  $\text{PE}_{(\text{OBS})}$  has a different sign (+, 0, or –) and is greater than  $\text{PE}_{(\text{HTA})}$ . Sets 2–4 correspond to pulse modes where  $\text{PE}_{(\text{OBS})} = \text{PE}_{(\text{HTA})}$  and data Set 5 corresponds to pulse modes where  $\text{PE}_{(\text{OBS})} < \text{PE}_{(\text{HTA})}$  and has a different sign. The relevance of grouping the three separate combinations of Set 1 together, and likewise, those of Set 5 (Table 3), lies in the assumption that similar effects create such observations. For example, in the case of Set 1, the degradation rate of OBS is always greater than the chemical activity in the system (i.e.,  $\text{PE}_{(\text{OBS})} > \text{PE}_{(\text{HTA})}$ ) and it is conceivable that the observations described by Subsets 1a–c (Table 3) occurred for similar reasons. The grouping of Set 5 (Table 3) follows similar logic. Representative pairs of  $\text{PE}_{(\text{OBS})}$ : $\text{PE}_{(\text{HTA})}$  data that fit into one of the sets shown in Table 3 have been highlighted in Figs. 6 and 7. By grouping similar data in this way, broader generalizations can be made on the effect of pulsing on bubbles.

Yang et al. [11] studied the sonochemical degradation of OBS at ultrasound frequencies of 206, 354, 620, 803 and 1026 kHz. At the frequencies of 620 kHz they found no evidence of positive  $\text{PE}_{(\text{HTA})}$ . However, for 616 kHz sonolysis in the current study all of the HTA formation rates had positive PE values under all pulse modes (Fig. 6b).<sup>1</sup> Although it is not possible to determine conclusively why positive  $\text{PE}_{(\text{HTA})}$  was observed at all sonication modes at 616 kHz in our work, a number of plausible explanations for this observation exist. First, during continuous wave ultrasound, bubble clusters may form [46] that prevent bubbles on the inside of the cluster from adsorbing enough energy to become sonochemically active cavitation bubbles. Additionally, the relatively close vicinity of bubbles to one another may result in an increase in bubble coalescence [43], resulting in the formation of bubbles that are larger than the resonant radius and are therefore sonochemically inactive [43]. However, by pulsing the ultrasound wave these clusters may be dispersed and coalescence may be reduced thereby allowing a greater population of bubbles to become sonochemically active [17], leading to positive  $\text{PE}_{(\text{HTA})}$  values.

In comparing  $\text{PE}_{(\text{HTA})}$ – $\text{PE}_{(\text{OBS})}$  at 616 kHz (Fig. 6), the number of possible data sets is limited to Sets 4, 5a and 5b (Table 3), since all  $\text{PE}_{(\text{HTA})}$  values were positive (Fig. 6). A positive  $\text{PE}_{(\text{HTA})}$  value indicates that pulsing has resulted in an increase in OH radical formation. Therefore, the positive  $\text{PE}_{(\text{OBS})}$  values observed at 616 kHz (for example, Fig. 6a, closed oval at  $T:T_0 = 60$  ms:320 ms) are attributed to increased oxidation of the surfactant by OH radicals due to changes in cavitation bubble populations with pulsing. However, data obtained at 205 kHz (Fig. 7) show that enhanced sonochemistry

<sup>1</sup> The discrepancy in this data at 616 kHz to that observed by Yang et al. [11] may be attributed to differences in volume sizes, power inputs, reactor dimensions and/or time of sonication used in the previous study. Thus, direct comparisons of the current study to the data in Yang et al. [11] are not possible.



**Fig. 6.** PE values for (a) degradation of OBS and (b) formation of HTA under various pulsed ultrasound conditions ( $f = 616$  kHz,  $P = 27$  W), relative to continuous wave ultrasound (i.e., the dashed line). The 95% confidence interval for the pulsed enhancement values were generated from the  $k_{\text{weighted}}$  values (Table 1 and 2) within each pulsed setting as compared to that of the continuous wave setting and have been marked with the upper and lower bound bars that were calculated using propagation of errors analysis.

as determined by the HTA formation rates is not the only parameter responsible for pulse enhanced OBS degradation.

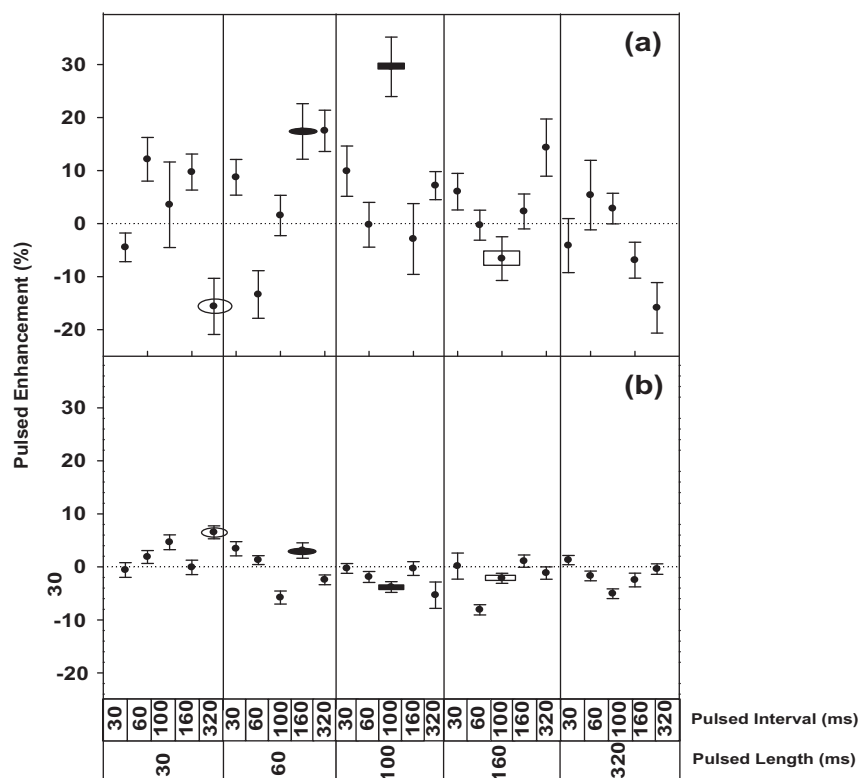
At 205 kHz and  $T:T_0 = 100$  ms:100 ms (Fig. 7, closed rectangles), Set 1b (Table 3) is observed. In this case a large positive  $PE_{\text{(OBS)}}$  value was observed under conditions where the sonochemical activity in the system decreased under pulsing (i.e.,  $PE_{\text{(HTA)}} < 0$ ). In this case the sonochemical activity in the system clearly is not a measure of the ability of ultrasound to decompose surface active organic solutes in aqueous solutions. The observation is of great practical interest since it shows that efficiency of sonochemical degradation of surface active contaminants in aqueous solutions are dramatically enhanced by pulsing the ultrasound wave, even under pulsing conditions that result in a decrease in sonochemical activity in the bulk solution.

Similar to Yang et al. [11], the plausible explanation for data that fall into Set 1b is that enhanced adsorption of OBS to the gas/solution interface of cavitation bubbles results in enhanced thermal and radical decomposition of OBS. The amount of surfactant that adsorbs to the gas/solution interface of cavitation bubbles depends not only on the thermodynamic adsorption properties of the surfactant, but also on its kinetic rate of adsorption [20]. Pulsing the ultrasonic wave increases the bubble lifetime and/or the lifetime of the gas/solution interface, thereby giving more time for surfactants to adsorb to the bubble interface, compared to continuous wave ultrasound. In addition to enhanced thermal and radical decomposition processes, the presence of OBS at the bubble interface stabilizes bubbles during the pulse interval,  $T_0$ , and inhibits dissolution due to a reduction in the Laplace pressure [11,20]. Electrostatic repulsion between bubbles with anionic surfactants adsorbed on surfaces (i.e., OBS) results in enhanced declustering

leading to more active bubbles through better adsorption of the ultrasound energy [19] and prevention of coalescence [43]. Enhanced adsorption processes only affect relatively long lived (stable) cavitation bubbles; therefore, a negative  $PE_{\text{(HTA)}}$  value at 205 kHz and  $T:T_0 = 100$  ms:100 ms (Fig. 7b, closed rectangle) is attributed to the comparatively hydrophilic nature of TA. A compound that does not adsorb to gas/solution interfaces is unable to prevent high-energy stable (HES) bubbles from dissolving during  $T_0$ . Therefore, OH radical formation is reduced due to the rapid dissolution or coalescence of stable bubbles (HES or otherwise).

Fig. 6 (616 kHz, closed squares) shows a decreasing PE for both OBS degradation rates and HTA formation rates at  $T = 30$  ms as  $T_0$  is increased from 30 to 320 ms, corresponding to sets 5a and b (Table 3). These observations show that a pulse length of  $T_0 = 30$  ms is long enough for sonochemically active bubbles to form. The gradual decrease in PE at longer  $T$  for both OBS degradation and HTA formation (Fig. 6, closed squares,  $T = 30$  ms) suggests that not all bubbles have enough time to grow to their resonance size and collapse, before starting to dissolve away during  $T_0$  due to Laplace pressure effects [17,23]. This explanation is consistent with the observed decreasing trends in PE at longer  $T_0$ , however it does not explain the observation that  $PE_{\text{(HTA)}}$  under these conditions was always a positive value (Fig. 6b, closed squares), compared to  $PE_{\text{(OBS)}}$ , which was almost exclusively a negative value (Fig. 6a, closed squares).

During  $T_0$ , it is expected that OBS will more readily adsorb to the gas/solution interface of cavitation bubbles compared to that during continuous wave ultrasound, leading to enhanced declustering, the prevention of bubble coalescence, and lower surface tension resulting in a decrease in the Laplace pressure inside the bubble.



**Fig. 7.** PE values for (a) degradation of OBS and (b) formation of HTA under various pulsed ultrasound conditions ( $f = 205$  kHz,  $P = 27$  W) relative to continuous wave ultrasound (i.e., the dashed line). The 95% confidence interval for the pulsed enhancement values were generated from the  $k_{\text{weighted}}$  values (Table 1 and 2) within each pulsed setting as compared to that of the continuous wave setting and have been marked with the upper and lower bound bars that were calculated using propagation of errors analysis.

**Table 3**

Comparative data sets, following the definitions of Yang et al. [11] for Sets 1(a), 2 and 3. Additional sets shown are described in the current work. '+' refers to a PE. '-' indicates a negative PE value (i.e., data points that lie below the 0% line in Figs. 6 and 7. '0' indicates that no PE was observed.

Set category	Pulse enhancement	
	OBS degradation	HTA formation
1a	+	0
1b	+	–
1c	0	–
2	0	0
3	–	–
4	+	+
5a	0	+
5b	–	+
5c	–	0

As discussed earlier, all of these effects would be expected to result in a greater  $PE_{\text{(OBS)}}$ , compared to the  $PE_{\text{(HTA)}}$ , yet the opposite was observed.

To understand this effect, the following a posteriori hypothesis is presented. When water is exposed to ultrasound above the acoustic cavitation threshold, a population of different types of bubbles is formed. Bubbles that produce sonochemistry are typically grouped into two categories, referred to as transient and HES bubbles [46]. As described by Sostaric and Riesz [20] and confirmed by Sunartio et al. [43], surfactants will not adsorb to the gas/solution interface of transient cavitation bubbles, since their lifetime is too short. Therefore, Sostaric and Riesz [20] concluded that all of the surfactants in their experiment dynamically adsorbed at rapidly pulsating surface of HES cavitation bubbles, over hundreds of acoustic cycles.

OBS, which adsorbs in significant concentrations at the surface of HES bubbles, undergoes thermal and free radical initiated decomposition at the surface of these bubbles. HTA, on the other hand, is formed by reaction in bulk solution of TA with OH radicals generated from both transient and HES cavitation bubbles. The observation that HTA formation rates are always enhanced during pulsing at 616 kHz (Fig. 6b) may be due to pulsing preventing clustering of relatively stable bubbles. The clustering of relatively stable bubbles leads to not only lower adsorption of ultrasonic energy by bubbles in the cluster center, but also to increased attenuation of the ultrasonic wave resulting in reduced formation of transient cavitation bubbles during continuous ultrasound. When pulsed, these clusters of stable bubbles have time to disperse during  $T_0$ . This results in decreased attenuation of the sound wave and allows for more transient cavitation bubbles to form during the successive 30 ms pulse.

HES bubbles on the other hand are severely affected by longer  $T_0$ . This is apparent from the negative PE that are eventually observed for OBS degradation rates at  $T_0 = 100, 160$  and  $320$  ms at  $T = 30$  ms (Fig. 6a, closed squares), because OBS adsorbs to and decomposes at the interface of HES bubbles [20,47].

Finally, HTA formation rates are similarly affected by the diminishing population of HES cavitation bubbles as  $T_0$  is increased at  $T = 30$  ms at 616 kHz (Fig. 6b, closed squares). However, because of the contribution of OH radicals that can react with TA in bulk solution from transient cavitation bubbles, HTA formation rates are always pulse enhanced, i.e., because of enhanced pulsing bubble populations due to declustering effects at all pulsing conditions, resulting in data sets 4, 5a and 5b (Table 3).

The proposed transient and HES bubble mechanisms used to describe the positive PE observed at  $T = 30$  ms (Fig. 6b, closed squares) for HTA formation are also valid at longer values of  $T$



considered in the current study at 616 kHz (Fig. 6b, all pulsed modes).

At 205 kHz and  $T:T_0 = 160\text{ ms}:100\text{ ms}$  (Fig. 7, open rectangle) the data represents Set 3 in Table 3. In this case both  $PE_{(\text{OBS})}$  and  $PE_{(\text{HTA})}$  were negative. Using the comparative method in the current study, little information is gained regarding the effect of pulsed ultrasound on this particular comparative data set, since a negative  $PE_{(\text{OBS})}$  may again be due to a number of variables, namely a decrease in the active cavitation bubble population during pulsing. It is interesting to note that of all of the pulsing conditions considered in the current study, data Set 3 is a very rare occurrence and only occurred for two pulsed conditions shown in Fig. 7 (i.e.,  $T:T_0 = 160\text{ ms}:100$  and  $320\text{ ms}:160\text{ ms}$ ).

#### 4.1. OBS degradation at extended sonolysis times

The sonochemical degradation of OBS was determined over relatively long sonolysis times at 616, 205 and 69 kHz (Figs. 1, 2 and 4) to investigate the effect of pulsing from a practical perspective. We chose to do this study under conditions where a positive PE was observed for the given pulsing condition, since this condition is of most interest from an energy efficiency perspective. It is interesting to note that the inflection point in the rate of OBS degradation during continuous mode sonolysis, which occurs at approximately 20, 15 and 150 min for 616, 205 and 69 kHz respectively, corresponds to approximately 6–7% degradation of the parent compound at all frequencies. This observation suggests that the formation and accumulation of byproducts in the bulk solution during sonolysis plays a role at all frequencies during CW exposure.

The result under CW ultrasound (Figs. 1, 2 and 4) is not without precedence. In sonochemical reactions in water, changes in the kinetics of the first-order degradation have been observed with increasing sonolysis time [1,36]. It has been suggested that this inflection of the initial first-order sonochemical rate of reaction to a slower, first-order sonochemical rate of reaction is due to the formation and accumulation of byproducts in the solution [15,48]. These byproducts act to compete with the parent compound for degradation ultimately slowing the kinetics of the initial first-order rate [15,48].

In contrast to the results at relatively long exposure times during CW ultrasound exposure, the rate of decomposition of the parent compound remained constant under all ultrasound conditions explored. This suggests that byproduct formation does not play a significant role in the rate of decomposition of the parent compound under pulsed ultrasound conditions.

Two possibilities for this behavior exist, depending on the nature of the degradation products. First, non-volatile byproducts formed at the surface of the bubble are expected to diffuse to and accumulate in the bulk solution. A portion of these byproducts may be molecules with surfactant properties that possess an *n*-alkyl chain that is shorter in length compared to the parent compound, and would therefore possess a lower thermodynamic affinity for the gas/solution interface of cavitation bubbles. However, because adsorption of surfactants to the gas/solution interface of cavitation bubbles is kinetically controlled [14,20,21], it can be expected that the byproducts possessing a shorter *n*-alkyl chain have a greater kinetic ability to reach and adsorb to the bubble surface. This competitive adsorption between the parent compound and shorter chain surfactants, results in a substantial decrease in the rate of degradation of the parent compound. Such an effect is not observed during pulsed ultrasound exposure, since the  $T_0$  is of sufficient time for the thermodynamically more surface active parent compound to adsorb more efficiently at the gas/solution interface of cavitation bubbles, compared to byproducts possessing a shorter *n*-alkyl chain.

Secondly, it is also likely that a portion of the byproduct formed is hydrophobic and/or volatile in nature (i.e., due to scission of the benzene sulfonate head group from the parent compound) [7]. The high hydrophobicity or volatility of these organics formed in the bubble would dictate that the majority of these compounds formed would tend to accumulate in the bubble over many collapse and growth cycles. Therefore, these byproducts have the potential to lower the temperature of the hot spot considerably, resulting in lower OBS degradation rates. For example, Ashokkumar et al. [49] reported that the ionization of gaseous hydrocarbons requires approximately 1000 kJ/mol of energy. In this study, as well as another by the same group [50], they reported that a small amount of hydrocarbon lowers the bubble temperature at collapse. It is further proposed, that during  $T_0$ , the bubbles will shrink to a smaller radius than during CW exposure. This resulting pressure build-up in the bubble forces gas out of the bubble and into the bulk solution, from where any excess hydrophobic and volatile components diffuse into the gas phase above the sample solution. In support of this hypothesis, it has been shown that volatile components [7,23] do accumulate in the head space of a sonochemical reactor in which aqueous solutions of organic solutes have been exposed to ultrasound. During the next ultrasound pulse, the bubble population re-grows, adsorbing dissolved gases that are in much higher concentration surrounding the bubble, compared to expelled volatile organic byproducts. Therefore, the effect of byproducts on decreasing the temperature of bubble collapse and therefore the rate of sonochemical degradation of the parent compound is only observed during CW ultrasound exposure.

## 5. Conclusions

Similar to earlier results comparing OBS degradation rates to HTA formation rates [11], no clear trends exist for the rates of these two sonochemical reactions as a function of ultrasound frequency and/or pulse mode. Differences in PE values between OBS and HTA are attributed to accumulation of OBS (but not TA) to cavitation bubble surfaces and changes in cavitation bubble dynamics under differing pulsing conditions. The results described above clearly show that pulsing affects the rate of degradation of aqueous surfactant solutions. In addition, using typical methods for determining sonochemical activity in water exposed to ultrasound (i.e., in this study TA/HTA) is not appropriate for predicting optimal pulsing conditions for degradation of surfactants. However, using this comparative method information is gained on how surfactants affect the cavitation process under different pulse mode and frequency conditions.

Experiments at extended sonolysis times revealed an important benefit of PW sonication. Under CW sonolysis, a clear inflection point in the first-order rate of degradation of OBS occurred, resulting in a substantial decrease in the first-order rate of degradation. Under PW sonolysis, however, the first-order rate of reaction was maintained and was greater than that observed under CW ultrasound. We hypothesize that PW ultrasound changes the internal composition of sonochemically active bubbles during pulse intervals, thereby creating hotter bubbles that contain less organic byproducts compared to bubbles under CW exposure.

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