# Degradation of Alkylphenol Ethoxylate Surfactants in Water with Ultrasonic Irradiation

3 AUTHORS, INCLUDING:

Michael R. Hoffmann
California Institute of Technology

**379** PUBLICATIONS **30,162** CITATIONS

# Degradation of Alkylphenol Ethoxylate Surfactants in Water with Ultrasonic Irradiation

HUGO DESTAILLATS,
HUI-MING HUNG, AND
MICHAEL R. HOFFMANN*

*W. M. Keck Laboratories, California Institute of Technology, Pasadena, California 91125*

During the last years, many efforts have been devoted to the elimination of alkylphenol ethoxylate surfactants from aqueous systems. In this paper, the sonochemical degradation of aqueous solutions of Triton X-100 was performed at an ultrasonic frequency of 358 kHz and an applied power of 50 W. Analysis of the reaction products by HPLC-ES–MS suggests that the hydrophobic alkyl chain is the preferential site for oxidation. Alkylphenol, or short-chain ethoxylated phenols, were not generated as byproducts. To verify this hypothesis, the sonochemical degradation of the corresponding alkylphenols (e.g., *tert*-octylphenol) was performed under the same conditions; in these cases, similar rate constants and products were observed. These results differ from those reported for the biodegradation of alkylphenol ethoxylates. A substantial increase in the rate constant was observed for the degradation of Triton X-100 below its critical micelle concentration. This observation indicates that micelle formation serves to effectively isolate the free surfactant monomers from the water–air interface of the oscillating cavitation bubbles, thus decreasing the overall efficiency of the sonochemical process. The hydrophobic tail of the molecule is no longer exposed directly to the bubble "hot spot" when it is pointed into the core of the micelles.

## Introduction

Surface-active compounds are discharged into domestic and industrial wastewater in considerable quantities, and as a consequence, they have become ubiquitous in the environment. Alkylphenol ethoxylates (APE) are a group of nonionic surfactants that have been used for many years as detergents, emulsifiers, and dispersing agents. Their environmental risks are the subject of much debate (*1*), since alkylphenols, which are produced during the biodegradation of APE, have been shown to have a higher toxicity, estrogenic activity, persistence, and tendency toward bioaccumulation than the parent substrate (*2–5*).

Several oxidative methods have been proposed for the remediation of water and wastewater effluents contaminated with APE. The majority of these methods focused on chemical or photochemical attack on the polyethoxylated chain and on the aromatic ring. For example, the fast ozonation of APE was studied and proposed as an efficient method for wastewater treatment (*6*), even though the principal product generated during ozonation is alkylphenol. Furthermore, the

total removal of organic matter is not achieved (*7, 8*). Heterogeneous and homogeneous photochemical reactions have been used for degradation of these surfactants (*9–11*). The radical especies ($^\bullet$OH, $^\bullet$HO$_2$) formed upon irradiation of the heterogeneous photocatalyst surfaces (e.g., TiO$_2$, WO$_3$, and MoO$_3$) reacted mostly with the ethoxylated chain of Triton X-100 (the adsorbed portion of the surfactant), producing short-chain carboxylic products, organic peroxides, hydroxylated compounds, alkylphenol, and mono- and diethoxylates. With sufficient time for continuous irradiation ($t_{1/2} = 150$ min), a reasonable degree of mineralization (measured as reduction of COD) was reached with that method. Brand et al. (*12*) investigated the homogeneous photochemical degradation of APE in alkaline solutions of Fe(III) at $\lambda < 300$ nm. The photoreduction of the metal center of the complex [Fe(H$_2$O)$_5$OH]$^{2+}$ yielded [Fe(H$_2$O)$_6$]$^{2+}$ and OH radical. The subsequent reaction of OH with APE produced alkylphenol, short-chain alkylphenol ethoxylates, formate ethoxylates, and aldehyde ethoxylates.

Ultrasonic irradiation has been shown to be effective for the treatment of chemical contaminants in aqueous solutions (*13–18*). The chemical effects of ultrasonic irradiation over the frequency range of 20–1000 kHz are the direct result of the formation of cavitation bubbles. Rarefaction and compression cycles induced by the ultrasonic pulses in the liquid generate cavities that grow until they reach a critical size and then due to resonant absorption of energy the bubbles undergo a violent collapse. The fast implosion of the cavitation bubbles produces a quasi-adiabatic heating of the vapor phase inside the cavity that yields localized high temperatures (thousands of K) and pressures. Water molecules under such extreme conditions undergo thermal dissociation to yield H and OH radicals. Organic solutes in the vicinity of a collapsing bubble or partitioned into the gas phase of the bubble undergo thermal decomposition and/or react with the reactive radicals. The purpose of this study is to demonstrate the technical feasibility of the degradation of APE in water under ultrasound irradiation. The chemical processes generated in the sonochemical reactor are able to operate on the different chemical features of these molecules, including the hydrophobic alkyl moieties.

Surface active molecules accumulate at interfaces, particularly at the water–air interface of the cavitation bubbles, and introduce major physical and chemical changes to their sonochemical response (*19–21*). Since cavitation bubbles are the "hot spots" where sonochemical reactions take place, surfactants should be particularly a good target for this treatment. Triton X-100 (TX, *tert*-octylphenoxy polyethoxyethanol) was chosen as a probe molecule for the degradation of APE surfactants by sonochemistry. Since the hydrophilic ethoxylated chains remain in the water surrounding the cavity, the alkyl chain is exposed to the extreme conditions reached during bubble collapse. Thus, both parts of the molecule are expected to undergo different sonochemical processes: the typical gas-phase reactions inside the cavity (pyrolysis) and the hydroxylation pathways characteristic of nonvolatile solutes in the typical sonochemical reactions (i.e., OH radical attack and addition). In this way, the degradation of surfactant molecules is achieved, and the generation of hazardous chemical byproducts, in principle, may be avoided.

## Experimental Section

Air-saturated aqueous solutions of TX were prepared in concentrations ranging from 17.1 to 632 ppm (about 0.03–1.13 mM, considering an average molecular weight of 558), above and below its critical micelle concentration (cmc $\simeq$

* Corresponding author phone: (626)395-4391; fax: (626)395-3170; e-mail: mrh@cco.caltech.edu.

**FIGURE 1.** UV spectra of the substrates employed in the sonochemical degradation and their changes with increasing irradiation time. $[TX]_0 = 0.035$ mM; $[TOP]_0 = 0.039$ mM. The fine lines belong to increasing irradiation times up to 90 min.

0.23–0.27 mM) (*9, 22*). The initial concentration was determined spectrophotometrically, through its absorbance at $\lambda = 224$ and 276 nm ($\epsilon_{224} = 8035$ and $\epsilon_{276} = 1228$ M$^{-1}$ cm$^{-1}$). Linearity of Lambert–Beer law was verified for the range of concentrations applied in this work (up to 1.25 mM for 276 nm and to 0.27 mM for 224 nm). Saturated aqueous solutions of 4-(*tert*-octyl)phenol (TOP) were prepared and filtered before irradiation to remove excess solid particles. The concentration of TOP was also established spectrophotometrically, its spectrum being very similar to that of TX ($\epsilon_{224}$ = 6898, $\epsilon_{278}$ = 1793, and $\epsilon_{196}$ = 39 680 M$^{-1}$cm$^{-1}$). The absorptivities determined experimentally for both TX and TOP in this work resulted quite comparable to the reported ones for Igepal CA 520, a commercial APE containing an average of $n = 5$ ethoxylate units (*12*). Thus, the presence of an ethoxylated chain of random length does not affect the apparent UV spectroscopic properties of these molecules, which originate in the aromatic group. Figure 1 shows the spectra of both substrates and their changes during sonication.

Sonochemical irradiation of the TX and TOP solutions was performed with an ultrasonic transducer USW 51 (AlliedSignal ELAC Nautik, Inc.) in a 600-mL glass and stainless steel reactor at 358 kHz with 50 W of input power (0.33 W/cm$^2$) and a constant temperature of 15 °C. Both

frequency and power are adjusted in a generator that is connected to the transducer. Sample aliquots (2.0 mL) were collected as a function of time for quantification by HPLC and identification by HPLC-ES–MS. The quantification of TX was performed with a Hewlett-Packard 1090 series HPLC with UV detection at 200, 230, and 250 nm, employing an ODS Hypersil HP C-18 column in reverse phase with a water– acetonitrile (50/50) mixture and a flow rate of 0.5 mL/min. Another column (MDS Hypersil, C-8) was used for quantification of TOP and also for product identification. The reduction in the actual concentration of the substrates, [TX] and [TOP], relative to their initial concentration, $[TX]_0$ and $[TOP]_0$, respectively, was calculated directly from the areas under their chromatographic peaks. Calibration over the range of concentrations employed showed a simple linear relationship in both cases. The same chromatographic conditions were employed for the qualitative analysis of the samples performed with an Hewlett-Packard 1100 HPLC system coupled to an electrospray mass spectroscopy interface (ES–MS). Positive ions were scanned from 50 to 2000 $m/z$ at 3 s/scan and skimmer cone voltage set at 3.5 kV, conditions that have been reported to be adequate for this kind of analytes (negative ion scanning proved to yield a much lower sensitivity for nonionic surfactants) (*22, 23*).

**TABLE 1. Pseudo-First-Order Rate Constants ($k_{-TX}$) and Half-Life Times ($t_{1/2}$) Determined for the Degradation of TX[a]**

| $[TX]_0$ (ppm) | $[TX]_0$ (mM) | $10^3 k_{-TX}$ (min$^{-1}$) | $t_{1/2}$ (min) | $[TX]_0 - [TX]_{60}$ (mM) |
|---|---|---|---|---|
| | | **Above cmc** | | |
| 632 | 1.13 (4.52 cmc) | 0.7 | 990 | 0.046 (4.1%) |
| 320 | 0.57 (2.28 cmc) | 1.0 | 693 | 0.033 (5.8%) |
| | | **Below cmc** | | |
| 62.7 | $1.12\ 10^{-1}$ (0.45 cmc) | 8.2 | 85 | 0.044 (39.2%) |
| 17.1 | $3.1\ 10^{-2}$ (0.12 cmc) | 21.5 | 32 | 0.023 (74.2%) |

[a] The amount of TX consumed during the first 60 min of irradiation ($[TX]_0 - [TX]_{60}$) was estimated with these parameters (cmc = 0.25 mM).

TX (Sigma, >99%) and TOP (Aldrich, >97%) were used as received, without further purification. All solutions were prepared with water purified by a Millipore Milli-Q UV Plus system ($R = 18$ MΩ·cm).

## Results and Discussion

The pseudo-first-order rate constant for TX degradation under the conditions of the present work, $k_{-TX}$, is defined in eq 1 as

$$-\frac{d[TX]}{dt} = k_{-TX}[TX] \tag{1}$$

The rate constant $k_{-TX}$ was calculated for four initial concentrations. These results are presented in Table 1 together with the reaction half-life times, $t_{1/2}$, defined in eq 2:

$$t_{1/2} = \frac{\ln 2}{k_{-TX}} \tag{2}$$

The rate constant for the degradation for a TOP solution ($[TOP]_0 = 0.04$ mM) was determined as $k_{-TOP} = 21.2$ min$^{-1}$. The solubility of TOP in water at 15 °C was estimated to be $0.053 \pm 0.008$ mM based on the spectrum of the saturated solution.

Figure 2 illustrates the different rates observed for the degradation of TX when the concentration is below and above the cmc as well as the results obtained for the degradation of TOP under the same irradiation conditions. The reaction rate in this latter case is quite similar to that observed for TX at the same initial concentration. This fact, together with the spectral behavior illustrated in Figure 1, suggests that the degradation processes for both substrates are similar.

The low $k_{-TX}$ values above cmc suggest that micelle formation reduces the apparent sonochemical efficiency by isolating the free surfactant monomers from the water–gas interface of the cavitation bubbles. Thus, micelles could be considered a good "shelter" from direct sonochemical effects. For concentrations below the cmc, the rate constants are comparable to those reported for other methods (9, 10). Over the range considered in this work, the rate constant increases for decreasing $[TX]_0$. This suggests that, even in the absence of micelles, the surfactant molecules be partitioned between the gas–liquid interface and the bulk liquid. Although rate constants vary over almost 2 orders of magnitude in the studied concentration range, the net reaction rate (i.e. moles per liter converted per unit time) does not show such dramatic change. Last column in Table 1 shows the estimated consumption of the substrate in the first 60 min of reaction, $[TX]_0 - [TX]_{60}$, indicating also the percentage of the total substrate reacted in each case. These values have been calculated by numerically solving eq 1 for each $[TX]_0$ and $k_{-TX}$ determined in the present work. The reaction rate depends, in principle, on the amount of free monomer available, which reaches a maximum in the presence of micelles, i.e., the cmc. Rates calculated for $[TX]_0$ below cmc are therefore higher than what a linear prediction would
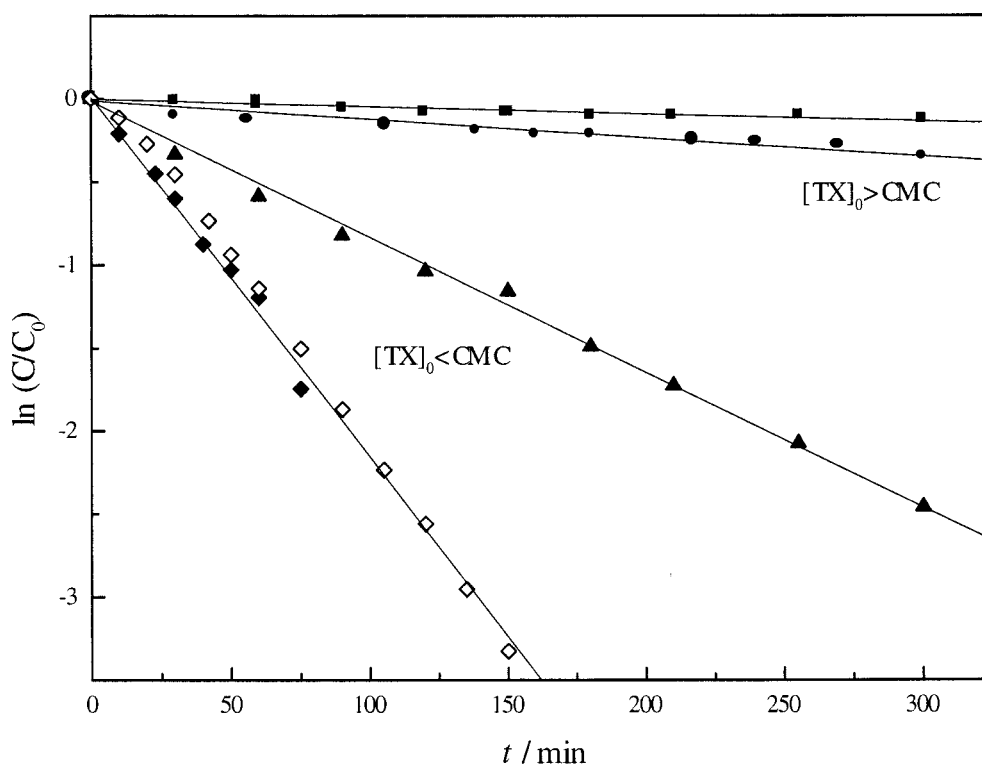


FIGURE 2. Sonochemical degradation of aqueous TX solution above and below cmc and of a TOP near-saturated solution. The dots represent the logarithm of the ratio between actual ($C$) and initial ($C_0$) concentrations. Straight lines show the best fit for TX. ■, $[TX]_0 = 1.13$ mM; ●, $[TX]_0 = 0.57$ mM; ▲, $[TX]_0 = 0.112$ mM; ◆, $[TX]_0 = 0.031$ mM; ◇, $[TOP]_0 = 0.039$ mM.
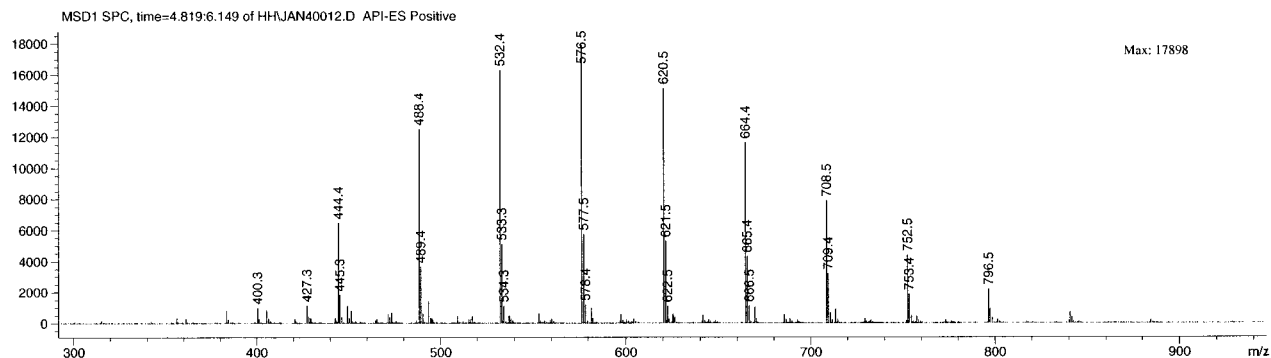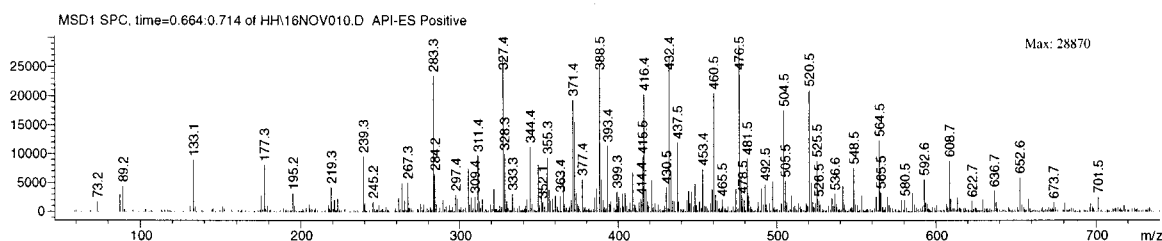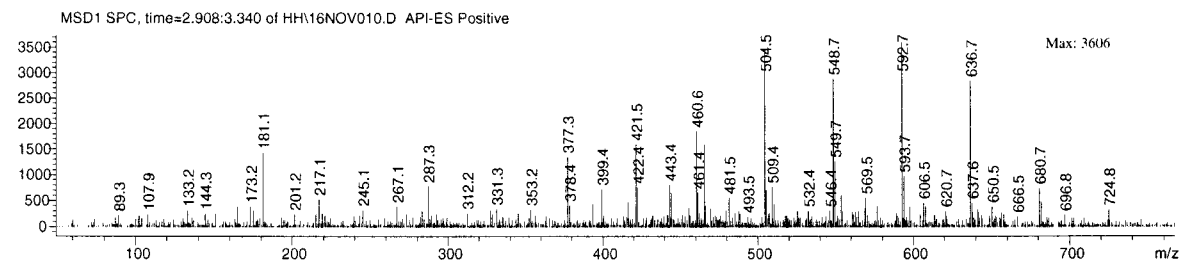
FIGURE 3. ES mass spectrum of TX. Chromatographic conditions: ODS Hypersil C18 column, water–acetonitrile (50/50), 0.5 mL/min. $T_r$ = 5 min.

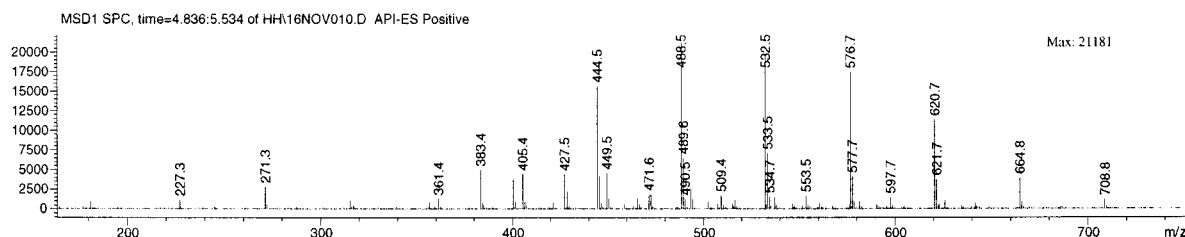(a) $T_r$ = 0.7 min



(b) $T_r$ = 3 min



(c) $T_r$ = 5 min (remaining reactant)
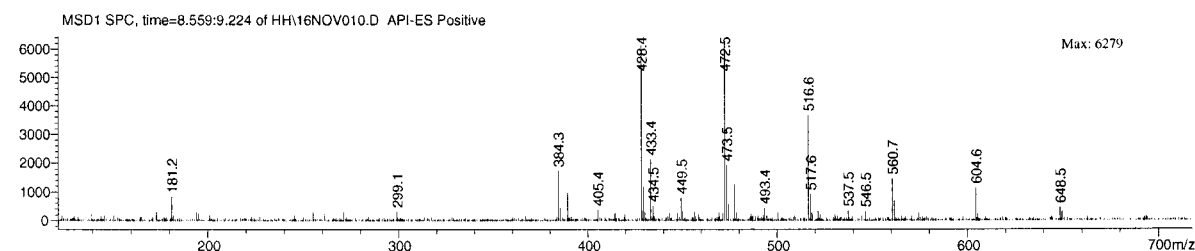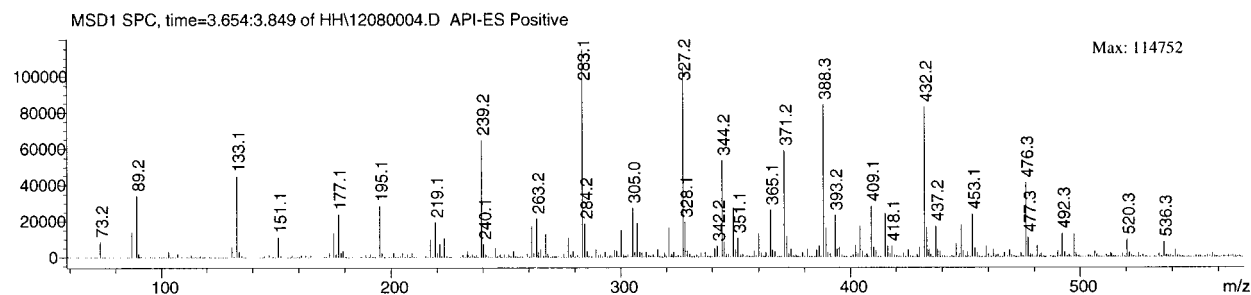


(d) $T_r$ = 8 min



FIGURE 4. ES mass spectra of the products originated in the sonochemical degradation of TX. Chromatographic conditions: ODS Hypersil C18 column, water–acetonitrile (50/50), 0.5 mL/min. Irradiation time: 300 min.

indicate, revealing other effects included on the pseudo-first-order rate constant, such as OH radical availability at each concentration. These effects were not observed in the ozonation studies performed by Ledakowicz and Perkowski (25). On the contrary, they reported a steady increase in the TX degradation rate by ozone for TX concentrations ranging

## (a) $T_r = 3.5 - 4$ min



MSD1 SPC, time=3.654:3.849 of HH\12080004.D API-ES Positive

## (b) $T_r = 4 - 4.5$ min



MSD1 SPC, time=3.963:4.158 of HH\12080004.D API-ES Positive
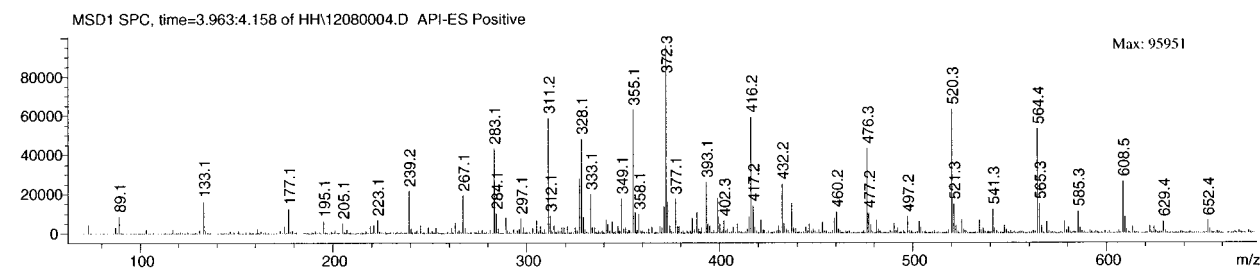
**FIGURE 5.** Resolution of the polar mixture at $T_r < 1$ with a different column. Chromatographic conditions: MOS Hypersil C8 column, water−acetonitrile (70/30), 0.5 mL/min. Irradiation time: 300 min.

from below cmc to the micelle region.

The product analysis performed by HPLC-ES-MS indicates that the alkyl chain in TX is the most reactive part of the surfactant molecule. Under the chromatographic conditions mentioned above, the original substrate solution (before sonication) shows a main single broad band with a retention time ($T_r$) of ca. 5 min, corresponding to the mixture of different number of ethoxylate units ($n$) of the surfactant molecules. The mass spectrum shown in Figure 3 shows a cluster of signals separated by 44 $m/z$, which corresponds to masses characteristic of the surfactant molecules ($M_{tx} = 206 + n44$, with $4 < n < 11$) and a water molecule attached to them. Assuming that mass discrimination effects are negligible, due to the similar nature of the compounds present in the sample, the cluster illustrates clearly the Poisson distribution of oligomers in the sample. The oligomers are generated during the synthesis of TX due to multiple ethoxylation of TOP. However, the oligomer with $n = 7$ is the most abundant one. Smaller peaks at ($M_{tx} + 1$) are due to protonation, and those between the main series are due to impurity Na$^+$ and K$^+$ ion attachment to the substrate molecules.
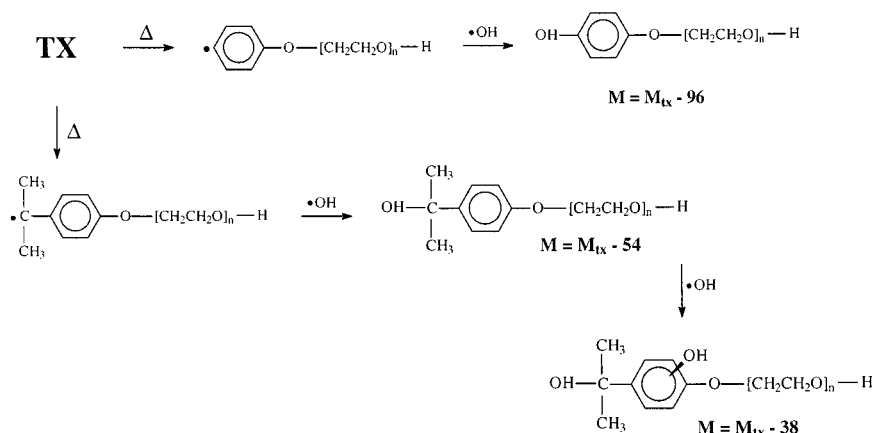
During sonication, the evolution of the reaction was monitored through the decay of the chromatographic peak of the substrate, while the appearance and increase of new bands are related to the byproducts that were also observed. The mass spectrum of the principal products mixture at a retention time $T_r = 0.7$ min (Figure 4a) shows a range of clusters of masses separated by 44 $m/z$, each with the same shape as the reactant cluster shown in Figure 3, revealing that these products still contain the ethoxylated structure. The main clusters in Figure 4a belong to the series $M = M_{tx} - 54$ (372.4, 416.4, 460.5, 504.5, 548.5, 592.6) and $M = M_{tx} - 38$ (344.4, 388.5, 432.4, 476.5, 520.6, 564.6, 608.7, 652.6) and cannot be correlated with any reasonable reaction occurring in the ethoxylated chain or in the aromatic ring. Any attempt to relate those products with the degradation of the alkyl chain must consider that reactions involving tertiary carbon radicals are the most favored. Thus, they may be attributed to the tertiary alcohols shown in Figure 6A. The cleavage in the bond linking the alkyl chain to the aromatic ring yields a polyethoxylated phenol with mass $M = M_{tx} - 96$. In this

case, odd masses of the cluster may include a hydronium H$_3$O$^+$ ion attached to the molecule (261.4, 305.4, 349.3, 393.4, 437.5, 481.5, 525.5). Together with these main clusters, fragments that originated in the polyethoxylated chain were also identified (239.2, 283.3, 327.4, 371.4). This group of peaks was observed in a systematic study of the ionization conditions at the skimer of the mass spectrometer (26) for the same type of APE and was found to be consistent with small parts of the polyethoxylated chain, hydroxylated, and attached to a H$^+$ ion [OH(CH$_2$CH$_2$O)$_n$H + H$^+$]. The peaks at $m/z = 89.2$, 133.2, and 177.3 belong to small (CH$_2$CH$_2$O)$_n$H fragments that might be generated during the electrospray ionization process. A protonated *tert*-pentanol can also be accounted for the peak at $m/z = 89$.
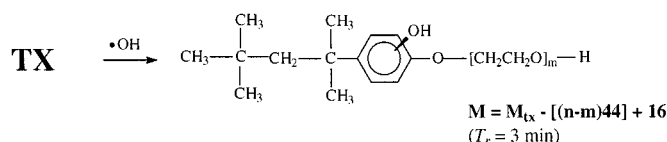
To confirm these hypotheses and to clarify the complicated MS signals shown in Figure 4a, other chromatographic runs were performed under different conditions, employing a column with higher polarity (MOS Hypersil) and different elution concentrations. Figure 5 illustrates some of these results. Although the mix of clusters on Figure 4a was not completely resolved, it was possible to classify them into two groups according to their elution time in different polarity conditions (70, 80, and 90% water concentration). The more hydrophilic $M = M_{tx} - 38$ cluster, together with the majority of the polyethoxylated fragments, always eluted first, and this behavior is consistent with the structures proposed in Figure 6A for the products of the degradation of TX based on oxidation of the alkyl groups.

Considering the minority products, the mass spectra of the species with $T_r = 3$ min (Figure 4b) was assigned to the product generated by OH radical addition to TX, presumable to the aromatic ring (Figure 6B), since the signals at $m/z = 460.6$, 504.5, 548.7, 592.7, 636.7, and 680.7 agree with the general formula $M = M_{tx} + 16$ (also with a water molecule attached). The radical attack on the polyethoxylated chain may generate different products, including short-chain polyethoxylated phenols, formates, and aldehydes (12). A small amount of short-chain APE generated in the reaction is indistinguishable from the substrate signals, since their masses are $M = M_{tx} - [(n - m)44] = M_{tx}'$ (same MS output, with $m \leq n$) and are not separated in the chromatographic

A) PRODUCTS OF THE PYROLYSIS OF THE ALKYL CHAIN ($T_r = 0.7$ min)

TX $\xrightarrow{\Delta}$ ... $\xrightarrow{\cdot OH}$ ...

$M = M_{tx} - 96$

$\downarrow \Delta$

... $\xrightarrow{\cdot OH}$ ...

$M = M_{tx} - 54$

$\downarrow \cdot OH$

$M = M_{tx} - 38$

(B) OH RADICAL ADDITION TO THE AROMATIC RING

TX $\xrightarrow{\cdot OH}$ ...

$M = M_{tx} - [(n\text{-}m)44] + 16$
($T_r = 3$ min)

(C) OH RADICAL ATTACK TO THE POLYETHOXYLATED CHAIN

TX $\xrightarrow{\cdot OH}$ $H_{17}C_8$—...—[O—$\overset{\cdot}{C}HCH_2$]-----

$+ H_2O$

$\downarrow O_2$

$H_{17}C_8$—...—[O—$\overset{\cdot}{C}HCH_2$]-----

$H_{17}C_8$—...—O—[$CH_2CH_2O$]$_m$—H

$M = M_{tx} - [(n\text{-}m)44] = M_{tx}'$
($T_r = 5$ min)

$H_{17}C_8$—...—O—[$CH_2CH_2O$]$_m$—CH$\overset{O}{\parallel}$

$M = M_{tx} - [(n\text{-}m)44] - 16$
($T_r = 8$ min)
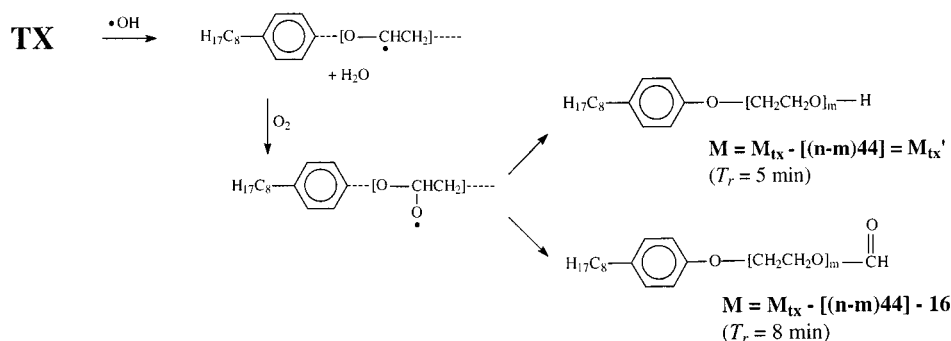
**FIGURE 6. Products generated in the sonochemical degradation of TX.**

run, having the same interaction pattern as the substrate molecule. Sherrard et al. (11) were able to follow the course of the photodegradation of APE in $TiO_2$ water suspensions by monitoring the shift to smaller masses of the envelope of ES—MS peaks taken at various irradiation times. During sonochemical degradation instead, the shape and retention time of the substrate band at $T_r = 5$ min is not changed after sonication, and no shift to smaller masses is observed in its MS cluster signals (see Figure 4c, with maximal signal still for $n = 6$ and 7). Thus, this chain-shortening pathway, which is very important in ozonolysis and in the photochemical methods, does not appear to be a relevant mechanism in the sonochemical degradation performed under conditions employed in this study. The same conclusion can be reached for most of the other products generated in the oxidation of the ethoxylated chain (i.e., they are near totally absent after sonochemical treatment). The small chromatographic signal at $T_r = 8$ (Figure 4d) is probably related with one of these minor products, such as formate ethoxylate (see Figure 6C), whose polarity is smaller than that of the original substrate. The MS cluster for this eluted fraction (384.3, 428.4, 472.5, 516.6, 560.7, 604.6, and 648.5), with general formula $M = M_{tx} - [(n - m)44] - 16$, agrees with the mass of these formate ethoxylates with a water molecule attached. Thus, sum-

marizing these experimental evidences, Figure 6 shows the mechanisms proposed for the sonochemical degradation of TX. The main reaction involves the pyrolytical cleavage of the alkyl chain under bubble collapse followed by combination with OH radicals produced in the same process (Figure 6A). Other reactions observed were the OH radical addition to the aromatic ring (Figure 6B) and the OH radical attack to the polyethoxylated chain, conducing either to a shorter polyethoxylated chain or to oxidized products (Figure 6C). These minor processes can also occur in the bulk solution with OH radicals released by the cavitation bubbles.

Some of the products generated in the degradation of TOP were also identified with ES—MS. For example, some peaks can be attributed to *tert*-octyl alcohol (with and without a water molecule attached, 130 and 148 $m/z$, respectively), *tert*-pentanoic acid (102 $m/z$), and a protonated aromatic aldehyde ($m/z = 165$). Due to the low concentration of TOP and its degradation products, the ES—MS technique was not able to detect some other molecules present in the samples. Nevertheless, the observed products suggest the existence of many reaction sites on the molecules that yield an array of different oxidation products.

The sonochemical degradation of TX was achieved at relatively fast rates as compared with some photochemical

methods previously reported (*9, 12*). *tert*-Octylphenol was not found to be a byproduct of the sonochemical degradation of TX, since its mass signal was absent in every chromatographic band analyzed in this study. On the contrary, the alkyl chain proved to be the most reactive part of the molecule, yielding highly soluble long-chained polyethoxylated phenols and alcohols, that can potentially undergo further rapid oxidation and/or biodegradation. These results were confirmed after sonochemical treatment of TOP aqueous solutions, which yielded similar products at similar rates. The micellar shielding observed for concentrations above the cmc suggests the important role played by the alkyl chain in the overall sonochemical degradation process.

## Literature Cited

(1) Renner, R. *Environ. Sci. Technol.* **1997**, *31*, 316 A.

(2) Giger, W.; Brunner, P. H.; Schaffner, C. *Science* **1984**, *225*, 623.

(3) Jobling, S.; Sumpter, J. P. *Aquat. Toxicol.* **1993**, *27*, 361.

(4) Jones, F. W.; Westmoreland, D. J. *Environ. Sci. Technol.* **1998**, *32*, 2623.

(5) Rudell, R. A.; Melly, S. J.; Geno, P. W.; Sun, G.; Brody, J. G. *Environ. Sci. Technol.* **1998**, *32*, 861.

(6) Delanghe, B.; Mekras, C. I.; Graham, N. J. D. *Ozone Sci. Eng.* **1991**, *13*, 639.

(7) Narkis, N.; Schneider-Rotel, M. *Water Res.* **1980**, *14*, 1225.

(8) Calvosa, L.; Monteverdi, A.; Rindone B.; Riva, G. *Water Res.* **1991**, *25*, 985.

(9) Dube, S.; Nageswara Rao, N. *J. Photochem. Photobiol. A* **1996**, *93*, 71.

(10) Pelizzetti, E.; Minero, C.; Maurino, V.; Sciafani, A.; Hidaka H.; Serpone, N. *Environ. Sci. Technol.* **1989**, *23*, 1380.

(11) Sherrard, K. B.; Marriott, P. J.; Gary Amiet, R.; McCormick, M. J.; Colton, R.; Millington, K. *Chemosphere* **1996**, *33*, 1921.

(12) Brand, N.; Mailhot, G.; Bolte, M. *Environ. Sci. Technol.* **1998**, *32*, 2715.

(13) Kotronarou, A.; Mills, G.; Hoffmann, M. R. *Environ. Sci. Technol.* **1992**, *26*, 2420.

(14) Hua, I.; Hochemer, R.; Hoffmann, M. R. *J. Phys. Chem.* **1995**, *99*, 2335.

(15) Hua, I.; Hoffmann, M. R. *Environ. Sci. Technol.* **1996**, *30*, 864.

(16) Hua, I.; Hoffmann, M. R. *Environ. Sci. Technol.* **1997**, *31*, 2237.

(17) Kang, J.-W; Hoffmann, M. R. *Environ. Sci. Technol.* **1998**, *32*, 3194.

(18) Weavers, L. K.; Ling F. H.; Hoffmann, M. R. *Environ. Sci. Technol.* **1998**, *32*, 2, 2727.

(19) Stottlemyer T. R.; Apfel, R. E. *J. Acoust. Soc. Am.* **1997**, *102*, 1418.

(20) Yasui, K. *Phys. Rev. E* **1998**, *58*, 4560.

(21) Ashokkumar, M.; Hall, R.; Mulvaney, P.; Grieser, F. *J. Phys. Chem. B* **1997**, *101*, 10845.

(22) Majhi, P. R.; Moulik, S. P. *Langmuir* **1998**, *14*, 3986.

(23) Scullion, S. D.; Clench, M. R.; Cooke M.; Ashcroft, A. E. *J. Chromatogr. A* **1996**, *733*, 207.

(24) Di Corcia, A. *J. Chromatogr. A* **1998**, *794*, 165.

(25) Ledakowicz, S.; Perkowski, J. *Inz. Chem. Procesowa* **1998**, *19, 1*, 205.

(26) Sherrard, K. B.; Marriott, P. J.; McCormick, M. J.; Colton, R.; Smith, G. *Anal. Chem.* **1994**, *66*, 3394.