

Sonochemical Degradation of a Polydisperse Nonylphenol Ethoxylate in Aqueous Solution

K. Vinodgopal,[†] Muthupandian Ashokkumar, and Franz Grieser**Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne, Parkville, VIC 3010, Australia**Received: November 13, 2000*

The ultrasound (363 kHz) induced decomposition of a commercially available polydisperse nonylphenol ethoxylate surfactant (Teric GN9) has been investigated. The initial rate of decomposition was found to be a function of the monomer concentration of the surfactant below and above the critical micelle concentration. Based on HPLC, TOC, GC, and sonoluminescence quenching measurements, we conclude that the initial pathway for the decomposition of the Teric GN9 occurs via a combination of thermal breakdown and radical attack on surfactant molecules adsorbed at the surface of cavitating bubbles. Nearly 90% mineralization and/or degradation into volatile products of the surfactant was achieved after sonication for 24 h.

Introduction

Nonylphenol ethoxylates (NPEs) form a class of very common ethylene oxide based nonionic surfactants with a wide variety of uses ranging from household to industrial applications.^{1,2} The popularity of these surfactants is attributable to the combination of the hydrophilic ethylene oxide chain, of variable length, with the hydrophobic alkyl chain, thereby making them versatile enough for an infinite number of applications. This popularity and the fact that these surfactants have been around for almost half a century means that they are also widely dispersed in the environment, creating an ever increasing concern about the ecological consequences of such a wide presence.

The ease of biodegradation of NPEs is inversely proportional to the degree of branching in the hydrophobic alkyl chain.³ In general, NPE degradation products, such as nonylphenol substituents are found under anaerobic conditions only and usually do not undergo any further biodegradation.^{4,5} The degradation products, particularly the nonylphenol are in general more environmentally catastrophic than the parent NPE. They are fat-soluble and therefore bioaccumulate^{6,7} and have also been implicated as environmental “estrogens”.⁸

NPEs can undergo chemical degradation, primarily via autoxidation at the ether linkages resulting in the formation of hydroperoxides and eventually shorter chain aldehydes and acids.⁹ A number of groups have studied the OH radical initiated photodecomposition of NPEs.^{10,11} Pelizzetti et al.¹⁰ have reported the complete mineralization of NPEs using TiO₂ photocatalysts, while Brand et al.¹¹ have reported their efficient degradation using OH radicals generated from the photolysis of Fe(III)–aquo complexes.

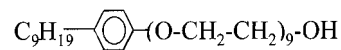
In recent years, a wide range of studies have shown that ultrasound-induced cavitation of aqueous solutions containing organic pollutants is an effective method for their destruction.^{12,13} The phenomenon of acoustic cavitation involves the formation, growth and eventual implosion of tiny gas bubbles.^{14–16} The violent collapse of the bubbles leads to near adiabatic

heating of the gas and vapor inside the bubble. This in turn leads to very high local temperatures and pressures commonly referred to as “hot spots”. In the case of aqueous solutions, these extreme conditions can lead to the homolysis of water molecules in the collapsing bubble to produce highly reactive H and OH radicals as well as other secondary oxidants.^{17–19}

In addition to radical formation through cavitation, which can be expected to degrade pollutants, such as the nonylphenol ethoxylates in aqueous solution, there is enough evidence accumulated from other basic studies in the phenomenon of cavitation to indicate that thermal pyrolysis can also be an important pathway for the destruction of compounds in aqueous solution. Several studies have shown that oxidative pyrolysis in the gas phase of the collapsing cavitation bubble plays a significant role in solute decomposition.^{17,20}

We have previously studied the effect of surface active agents, including surfactants, on sonochemical reactions and sonoluminescence, as a means of understanding the primary processes taking place at the bubble/solution interface during bubble collapse.^{21–23} It has been shown in these studies that for sonochemical reactions involving most nonionic organic solutes, the major determining factor in the rate of reaction is the interfacial concentration of the solute (i.e., the amount at the bubble/solution interface) and not directly the bulk concentration.

In this paper, we report on the sonochemical degradation of Teric GN9, a commercial nonylphenol ethoxylate surfactant and



present mechanistic details of the degradation process and some of the factors involved in achieving decomposition of the surfactant.

Experimental Section

Materials and Reagents. Polydisperse Teric GN9, a nonylphenol ethoxylate with an average of nine ethylene oxide (EO) units, was obtained from Orica Australia Pty Ltd. It is known that distribution of components of NPE surfactants, such as Teric GN9 follows a Poisson distribution. Nonylphenol (NP) was obtained from Kasei Chemicals. (Tokyo, Japan).

* Corresponding author: f.grieser@chemistry.unimelb.edu.au.

[†] Permanent address: Department of Chemistry, Indiana University Northwest, 3400 Broadway, Gary, IN 46408.

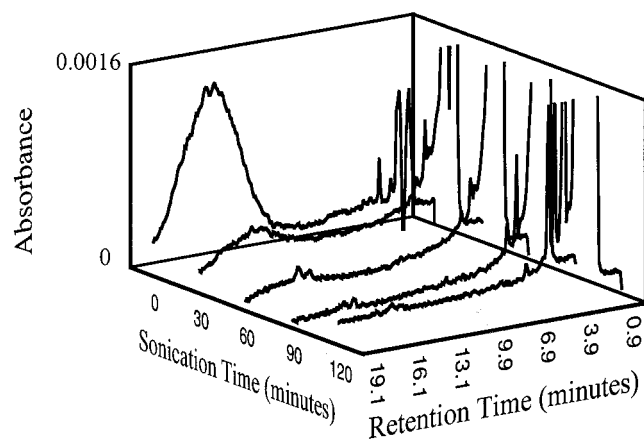


Figure 1. 3-D plot showing the evolution of the HPLC chromatogram as a function of sonication time. Mobile phase: acetonitrile/water (55:45 v/v) and detection wavelength = 226 nm. Initial surfactant concentration was 50 μ M. Sonication was carried out in an air-equilibrated solution.

Sonolysis. The ultrasound unit used for the degradation studies of the surfactant solutions was an Allied Signal (ELAC Nautik) RF generator and transducer with a plate diameter of 54.5 mm operated at 363 kHz in continuous wave mode. The effective power delivered to the solutions was 2 W/cm², as determined by calorimetry. The sonicating vessel used to contain the solution (200 mL) was jacketed, allowing cooling of the solution by passing cold water continuously through the jacket. All solutions remained exposed to the air atmosphere during sonication. Under these conditions the temperature of the solution remained between 20 and 30 °C throughout the sonication period.

Sonoluminescence experiments were carried out using the same experimental setup as for the sonochemistry work. Emission signals were detected with a Hamamatsu end-on photomultiplier and recorded on a Tektronics TDS 360 oscilloscope. All sonoluminescence experiments were carried out using 200 mL of solution and the temperature rise during the measurement time was less than 2 °C. (The initial solution temperature was 20 \pm 2 °C.)

Analytical Determinations. The reverse phase HPLC determinations were carried out on a Dionex model 300 system with UV detection at 226 nm using a standard C₁₈ Waters column (150 mm \times 3.9 mm i.d.) with an isocratic mobile phase of acetonitrile/water (55/45 v/v) flowing at 1.0 mL/min. Total dissolved organic carbon (TOC) measurements were made on an O. I. Analytical Instrument model 1010 using the wet oxidation method and appropriate standards. Electrospray mass spectroscopy (ESMS) measurements were made using a Micromass Quattro II ESIMS run at varying cone voltages using 50% acetonitrile/water as the eluent. GC analysis was made using a Shimadzu GC-8A gas chromatograph fitted with a FID detector; nitrogen was used as the carrier gas; the column used was a J&W GS Carbon Plot Capillary Column.

Results and Discussion

The degradation of the ethoxylate following sonication of air-equilibrated solutions at 363 kHz was monitored by HPLC and is shown in a 3-D plot in Figure 1. It has been assumed that the area under the entire peak is directly proportional to the concentration of the total Teric GN9 surfactant. Consistent with previous studies on the reverse phase HPLC separation of these NPEs, the shorter ethoxylate chain oligomers ($n < 9$), which are less hydrophilic, have the longer retention times in the

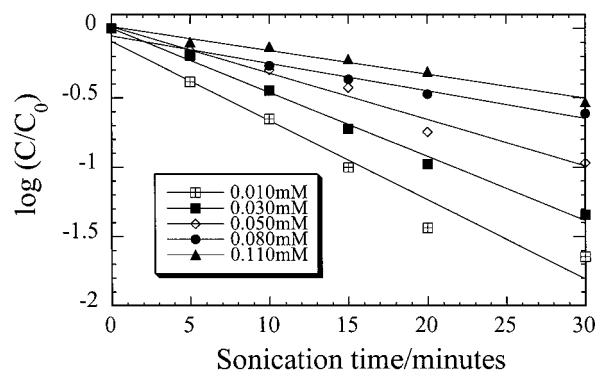


Figure 2. Decomposition of Teric GN9 as a function of sonication time at different initial surfactant concentrations. The decomposition of the Teric GN9 was monitored from the change in the area of the surfactant band in the HPLC chromatogram.

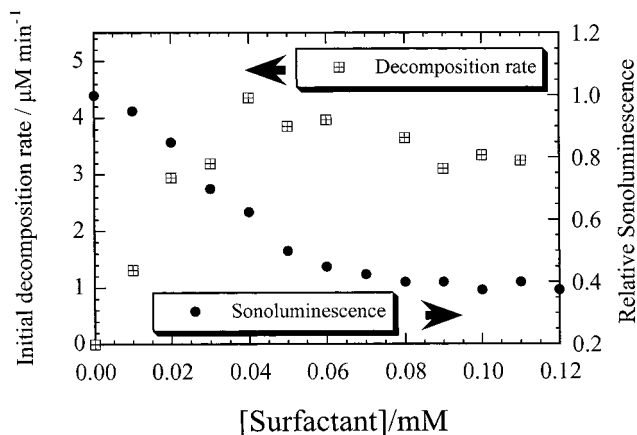


Figure 3. Initial decomposition rate of Teric GN9 as a function of initial surfactant concentration. Also plotted on the right Y-axis is the relative sonoluminescence emission intensity of these solutions.

observed band.^{11,24} The figure shows that as the NPE components are degraded, over about 2 h of sonication, a substantial increase in hydrophilic products, eluted at short retention times, occurs. More will be said on this later.

The extent of decomposition of the surfactant as a function of concentration is shown in Figure 2. The notable feature of this plot is that the decomposition of the surfactant is exponential with sonication time instead of an expected linear behavior. As the sonication time can be considered to be a measure of the applied power per solution volume (i.e., W/volume), it can be expected that the decomposition of the surfactant should exhibit zero-order kinetics. Indeed, zero-order kinetics have been observed for the degradation of organic solutes^{12,25} but first-order decomposition kinetics have also been reported.^{26,27} Generally if pyrolysis is involved in the decomposition process the reaction kinetics are first-order.²⁶ This point is of significance in interpreting the mechanism for the degradation of the Teric GN9, as will be discussed shortly.

The rate of the decomposition of the surfactant at different initial concentrations can be extracted from Figure 2. When the initial decomposition rates are plotted against the initial surfactant concentrations, as in Figure 3, the graph shows two distinct concentration regimes. The decomposition rate increases as the initial concentration increases from 10 to 40 μ M, reaches a maximum, and then declines slightly. The surfactant concentration at which the maximum decomposition rate is obtained corresponds closely to the critical micelle concentration (cmc) [$(5 \pm 1) \times 10^{-5}$ M] of Teric GN9.²⁸

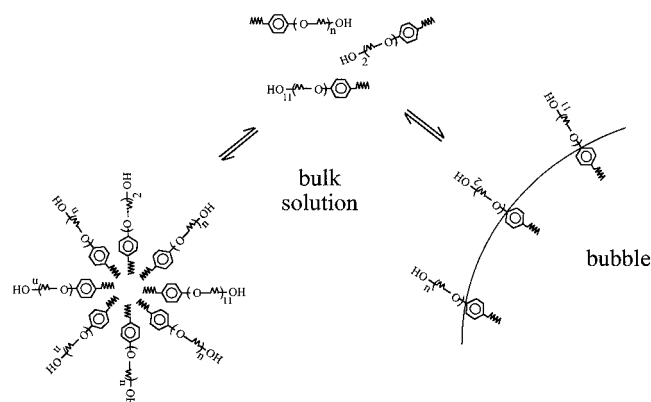


Figure 4. Representation of the equilibrium of individual components of Teric GN9 with mixed component micelles and the bubble/solution interface. The relative proportions of the components in solution, in the micelle, and at the interface will be dependent on the initial concentration of the surfactant.^{28a}

The almost constant decomposition rates²⁹ above the cmc and the sharp decrease in the rates with concentrations below the cmc strongly suggest that only surfactant in monomer form is involved in the decomposition reactions. On the basis of several studies of the effect of these surfactants at the air/water interface,³⁰ it has been concluded that the orientation of the surfactant at the bubble/solution interface is such that the ethoxy chain is directed toward the aqueous solution and the hydrophobic hydrocarbon portion of the surfactant is directed into the bubble. Such a scheme showing the monomer–micelle and monomer–bubble surface equilibria and the orientation of the polydisperse surfactant at the bubble/solution interface is illustrated in Figure 4.

Consistent with the above scheme, degradation of the surfactant then is primarily an interfacial event involving only the monomer form. Two possible degradation pathways exist: (a) direct thermal degradation of the surfactant in the hot interface¹⁶ of the cavitation bubble; (b) radical induced oxidation of the surfactant at the bubble surface. Once fragmentation of the surfactant has occurred, pyrolysis reactions within the bubble of volatile components can then be expected.

Tauber et al.²⁰ have shown in the sonochemical decomposition of *tert*-butyl alcohol that the reaction occurs almost entirely at or near the surface of the bubble. They report that an extensive array of products can be identified in the reaction of *tert*-butyl alcohol, some the result of radical induced decomposition and the others from pyrolysis within the bubble.²⁰ It is reasonable to postulate that a similar scenario exists in the case of the NPE surfactant with the exception that because Teric GN9 has essentially no volatility, its initial decomposition cannot take place within the bubble.

However, evidence to support the proposal that decomposition occurs at the interface and that at least some decomposition products enter the bubble is provided from our sonoluminescence experiments. The phenomenon of sonoluminescence is the broad wavelength emission of light occurring at the final stages of the ultrasound field-induced bubble collapse.¹⁴ The type of solute present in the liquid influences the intensity of the sonoluminescence.^{14,21–23} In recent work from this laboratory, it has been shown that the quenching of the sonoluminescence in aqueous solution by nonionic solutes is a direct function of their surface excess, i.e., the amount of the nonionic solute at the bubble/water interface.^{21–23} This appears to be the case for both multibubble and single bubble systems.³¹

The change in the sonoluminescence intensity of aqueous solutions of the Teric GN9 as a function of concentration is

shown in Figure 3 in order to compare with the dependence of the initial decomposition rate on concentration. The intensity of the emission has been normalized relative to the emission intensity observed in Milli-Q water. The change in the sonoluminescence intensity with concentration falls into two distinct regions, approximately separated by the cmc. Above the cmc, the emission intensity is approximately constant, reflecting the constant monomer concentration in solution, and hence surfactant concentration at the bubble/solution interface. The possibility that the presence of surfactant at the bubble surface affects the collapse of the bubble and hence the SL produced cannot be completely excluded. However, based on the results of experiments with a range of surface active solutes, the presence of solute at the surface of a bubble is not on its own sufficient to affect multibubble sonoluminescence.^{21,22} On the basis of our work on multibubble sonoluminescence quenching by surface active solutes,^{21–23} the observed quenching of the sonoluminescence by the nonylphenol ethoxylate is probably linked to the fragmentation of the surfactant at the surface of the bubble. The volatile hydrophobic decomposition products of the NPE are expected to build up in concentration within the bubble over many cycles of bubble expansion and compression.²² As the decomposition products accumulate within the bubble, the heat capacity ratio γ^* will decrease, and possibly P_g (the pressure within the bubble at the point of collapse) will increase, thereby lowering the bubble core temperature and hence the intensity of sonoluminescence as per eq 1,¹⁴ where

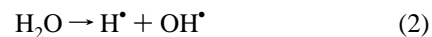
$$T_{\max} = T_0 P_a (\gamma^* - 1) / P_g \quad (1)$$

P_a is the pressure exerted on the bubble at the point of collapse, T_0 is the ambient temperature, and T_{\max} is the peak temperature generated on collapse. In addition, the presence of complex decomposition products within the bubble will mean that some thermal energy will be used in endothermic dissociation processes and this too will lead to lower core temperatures.²⁰

In essence, the sonoluminescence results indicate that the decomposition of the surfactant produces volatile products, the amount of which depends on the monomer concentration of the surfactant. The presence of these volatile gases within the cavitating bubble would also explain why zero-order kinetics are not observed in the initial degradation rate of the Teric GN9. Some of the volatile products were identified in a separate experiment where a Teric GN9 solution was sonicated in a sealed vial. Some of the gases trapped in the headspace of the vial were qualitatively identified by GC analysis as methane, ethane, propane, acetylene, and hydrogen.

To quantify the overall decomposition of Teric GN9, the TOC of the solutions was measured as a function of sonication time (Figure 5) for different initial concentrations of the surfactant. The TOC declines by almost 90% after prolonged sonication (24 h), indicating quite effective mineralization/production of volatile decomposition products. It is also relevant to recognize that while >95% of the Teric GN9 is decomposed in the first 2 h (e.g., Figure 1), there is a less than 10% decrease in the TOC in this time period. This indicates that the initial decomposition step of Teric GN9 primarily produces water-soluble components, which is consistent with the HPLC results in Figure 1 at short retention times.

In the radical induced decomposition of the surfactant, the initial step is the thermal dissociation of water in the collapsing bubble to produce OH radicals and H atoms given that water vapor is expected to be a major constituent of the bubble.



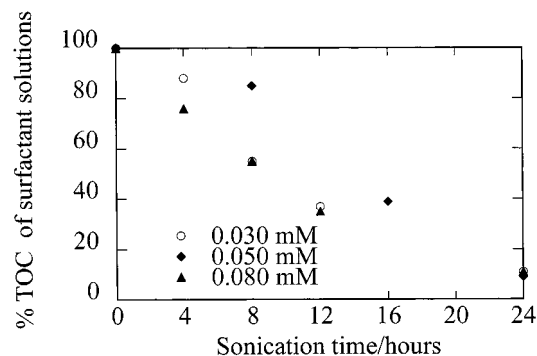


Figure 5. Total organic carbon (% TOC) content of Teric GN9 solutions as a function of sonication time for different initial surfactant concentrations. Sonication was carried out in air-equilibrated solutions.

A number of groups have shown that at the surface of the collapsing bubble, the OH radical concentration is quite high.^{17–20} While some of these OH radicals will recombine to give H₂O₂ via reaction 3, the rest can be expected to initiate



the oxidative degradation of the monomer surfactant also present at the bubble surface. Only a very small fraction of the OH radicals are expected to reach the bulk of the liquid. This is consistent with the observed concentration dependence of our surfactant decay rate. At concentrations above the cmc, the decomposition rate flattens out, as the monomer concentration at the surface of the bubble is approximately constant.

As indicated in the earlier studies of Pelizzetti et al.¹⁰ and Brand et al.,¹¹ there are three areas for possible OH radical attack on the surfactant: (a) the alkyl chain, (b) the aromatic ring, and (c) the ethoxylate chain. Brand et al. have proposed a detailed mechanism involving OH attack on the ethoxylate chain.¹¹ They proposed an initial H atom abstraction from the α -methylene groups on the ethoxylate chain, formation of alkoxy radicals and subsequent scission of C–O and C–C bonds within the ethoxylate chain leading to the formation of both alkylphenol and shorter alkylphenol ethoxylates. However, as Pelizzetti et al.¹⁰ have pointed out in their photocatalysis study, in the solution phase OH addition to an aromatic ring is considerably faster than hydrogen atom abstraction. Given the fairly high temperature at the bubble surface and the correspondingly lower activation barriers compared to bulk solution, it is likely that attacks on both the aromatic ring and the ethoxylate chain occur competitively.

Brand et al.¹¹ in their degradation study of alkylphenol ethoxylates reported the presence of the alkylphenol as an intermediate, while Pelizzetti et al.¹⁰ did not identify any alkylphenol. We have investigated the HPLC chromatogram obtained (under the same exact conditions as the ethoxylate surfactant) of a commercial sample of 4-nonylphenol with a view to determining whether this is indeed formed as an intermediate. Commercial 4-nonylphenol is a mixture of several isomers with branched alkyl side chains. Since nonylphenol is considerably more hydrophobic than the surfactant (corresponding to $n = 0$), its retention time is much longer than that of the surfactant. On the basis of the 4-nonylphenol standard, we did not see any evidence in our HPLC chromatograms for the formation of nonylphenol during the sonication of the Teric GN9. We have also looked at the ESMS spectra of sonicated NPE solutions and could not detect the presence of nonylphenol. Furthermore, the sonochemical degradation of phenols and substituted phenols have been well studied by a number of

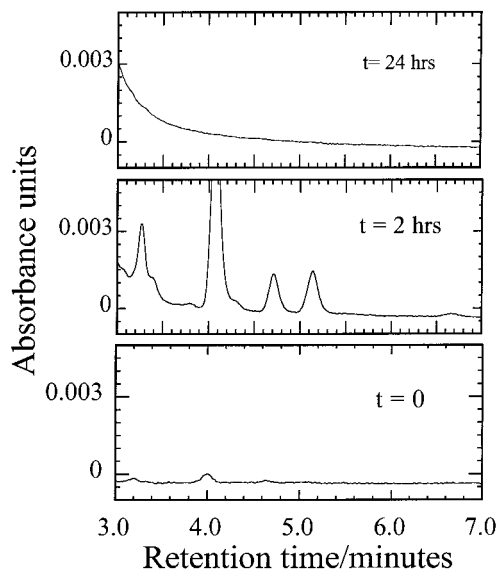


Figure 6. HPLC chromatogram recorded between the retention times of 3 and 7 min of a 50 μM solution of Teric GN9. The chromatograms were recorded (a) before sonication, (b) after 120 min of sonication, and (c) after 24 h of sonication. All solutions were air-equilibrated.

groups;^{12,13,32} however, due to the complexity of the chromatograms in our case, it was difficult to identify any nonylphenol decomposition products.

Attack on the ethoxylate chain resulting in chain shortening is also expected to produce low molecular weight poly(ethylene glycol) (PEG) as a byproduct. Henglein has studied the sonochemistry of poly(ethylene glycol)¹⁷ and has shown that it accumulates strongly at the bubble/water interface, and under an argon atmosphere, undergoes efficient pyrolysis in the cavitation bubble. It is also known from the radiation chemistry literature that poly(ethylene glycol)s react quite rapidly with OH radicals.³³

The HPLC chromatogram (Figure 6) obtained after 2 h of sonication shows several peaks that persist and only disappear after prolonged sonication. Brand et al.¹¹ have identified shorter chain formate ethoxylate esters as well as aldehyde ethoxylates as intermediates in their surfactant degradation scheme. In their case, however, they observed the formate esters at longer retention times, as these esters were derivatives of the surfactant backbone (i.e., the hydrocarbon chain and aromatic ring moiety). Despite the fact that our HPLC procedures are almost identical, we do not see any evidence of any intermediates at longer retention times. It is quite likely that at least some of the peaks that we observe in our chromatograms after sonication are species arising from the oxidation of the polyethoxy fragment of the surfactant. These would be expected to be more hydrophilic and therefore should have shorter retention times and persist for longer periods during ultrasound irradiation. Brand et al.¹¹ have observed bands at shorter retention times but have not identified them.

The pH of an air-equilibrated 50 μM Teric GN9 surfactant solution changes from 6.6 to 2.3 after 24 h of sonication, reflecting the formation of an acidic end product. Electrospray mass spectrometric measurements were undertaken to identify the species remaining after 24 h of sonication. These measurements indicated that the only ionizable organic species remaining in solution was oxalic acid, but they also revealed the presence of large amounts of the nitrate ion. The optical absorption spectrum of NO₃[−] shows absorption bands at 210 and 300 nm, the former being the more intense one. These bands correlate very well with those seen in the absorption spectra of the

sonicated surfactant solution. A substantial body of data available in the literature on the irradiation of air-equilibrated water with ultrasound shows that both nitrate and nitrite ions are formed as end products.^{13,17,34–38} Under the extreme conditions generated in the collapsing bubble, homolysis of oxygen and to a lesser extent nitrogen can occur. This is followed by the formation of nitric oxide, which subsequently reacts with OH radicals to produce HNO₂. What is noteworthy in our experiments is that we see no evidence of the nitrite ion following 24 h of sonication, most likely because it is converted to nitrate by reaction with H₂O₂³⁸ produced via reaction 3. The nitrate ion that is produced coelutes with the oxalic acid in our ion chromatographic and HPLC analyses. Consequently, we were unable to quantify the residual oxalic acid concentration after 24 h of sonication.

In summary, the present study shows that nonionic surfactants such as nonylphenol ethoxylates can be effectively degraded and mineralized/pyrolysed using ultrasound. The degradation process takes place initially at the bubble/solution interface by both thermal and radical reactions and subsequently via pyrolysis. We note that many of the conclusions drawn from our results are comparable to the results of a recent study by Destailats et al.³⁹ on the sonochemical degradation of Triton X-100, which is also an alkylphenol ethoxylate. In this latter study an electrospray MS analysis of the results provides additional evidence that the initial decomposition of alkylphenol ethoxylates occurs by both thermal decomposition and OH attack on the surfactant.

Acknowledgment. We thank Dr. Fuping Hao and Simon King of CSIRO, Australia, for their help with the HPLC and TOC measurements, respectively. We are grateful to Dr. Bob Bohun for providing the sample of Teric GN9. K.V. acknowledges a Visiting Scholars Award from the University of Melbourne. Support for this work from the Australian Research Council and the EC (COST Chemistry D10 program) is gratefully acknowledged.

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