

High-Temperature Stability of Alcohol Ethoxylates

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ABSTRACT: The oxidative stability of alcohol ethoxylates during storage and handling is studied. Realistic conditions are modelled by heating in quiescent air. More rigorous, extensively aerated conditions are modelled by thermogravimetry with mass spectrometric detection and differential scanning calorimetry with vapor-phase sampling.

In quiescent air, C₁₂₋₁₅ alcohol with an average of 7 moles ethylene oxide (EO) is discolored at 204°C, with some increase in aldehydes, but there is no change in the EO distribution of the sample. Under extensively aerated conditions, increased oxidation occurs above 150°C, with a loss of one EO unit on average, and increases in CO and CO₂ occur in the vapor phase above the sample. High-temperature oxidation under extensive aeration is not affected by an antioxidant or by raising the pH of the sample from 6.4 to 7.5.

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KEY WORDS: Alcohol ethoxylate, autoxidation, oxidation, polyoxyethylene chain, stability.

Alcohol ethoxylates are one of the most important families of nonionic surfactants. They are widely used in household and in industrial detergents and as processing aids in a variety of applications. Alcohol ethoxylates are manufactured by reacting an alcohol with ethylene oxide (EO) in the presence of a catalyst. Commercial alcohol ethoxylates are mixtures of various ethoxamers, differing in the number of EO units attached to the parent alcohol molecule. Changes in the catalyst system can change the distribution of EO units in the alcohol ethoxylate. The EO chain, frequently called the polyoxyethylene chain, imparts water solubility to the alcohol ethoxylate. Like all ethers, alcohol ethoxylates are susceptible to free-radical oxidation in the presence of air because of the activating effect of the etheric oxygen. Peroxo compounds are intermediates in this autoxidation (1,2), increasing in concentration during the propagation period and decreasing during the termination period (3-5). The stability of the polyoxyethylene chain toward oxidation has been extensively reviewed by Donbrow (6).

Autoxidation of alcohol ethoxylates is of continuing interest. Conditions leading to autoxidation, products of autoxidation,

and thermochemical characteristics of autoxidation are important considerations within the context of product stewardship and Responsible Care[®]. We report here work in which we examined the stability of alcohol ethoxylates under conditions of high temperature and high temperature and vigorous aeration, where significant oxidation is expected.

EXPERIMENTAL PROCEDURES

Samples. A C₁₂₋₁₅ alcohol with an average of seven moles of EO per mole of alcohol was used for this work. This was a commercial sample (NEODOL[®] 25-7; Shell Chemical, Houston, TX), produced by conventional basic catalysis and having a conventional EO distribution.

Autoclave heating. A sample was sealed in an autoclave with air at ambient temperature and pressure. The temperature was increased from ambient to 38°C (100°F), held for one hour, then increased in increments of 38°C (100°F) and maintained for one hour at each temperature, up to 204°C (400°F). Aliquots were withdrawn at the end of each one-hour hold period. Adequate nitrogen pressure to force the aliquots through a sampling tube was introduced for each aliquot withdrawal. Neat alcohol ethoxylate and alcohol ethoxylate mixed 50:50 vol/vol with water were studied. Formaldehyde and acetaldehyde levels and ethylene oxide adduct distributions (EOD) were determined for these samples in an attempt to correlate changes in EOD with increases in the aldehydes.

Aldehyde determinations. Formaldehyde and acetaldehyde were determined by reaction with para-nitrobenzyloxyamine to form the corresponding oximes at pH 4.4, followed by chromatographic separation of the oximes and detection by ultraviolet (UV) spectrophotometry at 267 nm. The column was a C₁₈ bonded-phase column, 250 mm × 4.6 mm i.d., with 5-micron particle size. The mobile phase was 58:42 acetonitrile/0.1% dibasic ammonium hydrogen phosphate solution, flowing at 1.5 mL/min. Cyclohexanone was used as an internal standard for quantitation.

EOD. EOD for the alcohol ethoxylates were determined with a two-step combined gas chromatography (GC)/liquid chromatography (LC) technique. The GC technique covers the EO₀ to EO₈ ethoxamers; the sample is converted to the trimethylsilyl derivative and run in a DB5 15 × 0.32 mm i.d.

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column (J&W Scientific, Folsom, CA) with 0.1 μ film thickness. Helium was used as the carrier gas. The temperature program was 100 to 320°C at 5°C/min, and a 16-min hold at 320°C to elute heavy ends. Detection is by flame-ionization.

The LC technique covers the EO₅ to EO₃₀ ethoxamers. The sample was converted to the phenylisocyanate derivative and run in an SI-5 25 cm \times 4.6 mm i.d. column (Supelco, Inc., Bellefonte, PA), with 10- μ L injection. Gradient elution was used with a ternary mobile phase composed of acetonitrile, methanol, and isopropanol. Detection was by UV spectrophotometry at 240 nm.

The EO₆ ethoxamer, which is present in both measurements, is used to normalize and combine the two chromatograms into a single distribution.

Thermogravimetry. Thermogravimetry was carried out on a DuPont (Boston, MA) 951 thermogravimetric analysis (TGA) coupled to a Hewlett-Packard (Palo Alto, CA) 5971A Mass Selective Detector (MSD) with a fused silica splitter interface. Sample temperature was increased stepwise from ambient to 260°C, holding at five intermediate temperatures for 30 min each. Three steps of approximately 20°C were used between 149 and 204°C. The MSD was scanned from 15 to 550 Daltons. Helium and air were used as carrier gases, the former to understand volatilization, the latter to study oxidation. Carrier gas flow rates from 10 to 50 mL/min were used; no differences were noted as a function of carrier gas flow rate.

Calorimetry. Measurements were made in a Setaram C-80 microcalorimeter (Societe d'Etudes d'Automatisation de Regulation et d'Appareils de Mesures, Claire Cedix, France). Six to seven grams of sample were placed in both the reference and the sample cells. The material in the reference cell was sealed under house N₂ at ambient pressure while the material in the sample cell was sealed under ambient air. Samples were heated from room temperature to 204 at a constant rate of 0.5°C/min.

Calorimetry in unsealed cells, with air and nitrogen flowing through the samples at 50 mL/min, was unsuccessful, because heat was irreproducibly transferred through the open, flowing gas system. However, this attempt provided an opportunity to study other effects of vigorous aeration with heating; samples of the flowing air were taken and analyzed by GC and selective gas sampling tubes, and samples of the residual material were withdrawn after heating and aeration for analysis.

RESULTS

Calorimetry. Results for calorimetry of an alcohol ethoxylate sample in a static air atmosphere are given in Figure 1. For temperatures up to 200°C, there was minimal evidence for any thermochemical reaction. Around 130°C there is a mild exothermic reaction, indicated by the "wave" in the horizontal line on the plot. Given the sample mass (approximately 7.3 g), the heat capacity of ethoxylated linear primary alcohols (approximately 0.5 calories/gram/°C) and the measured power generated in the sample (given by the ordinate), the

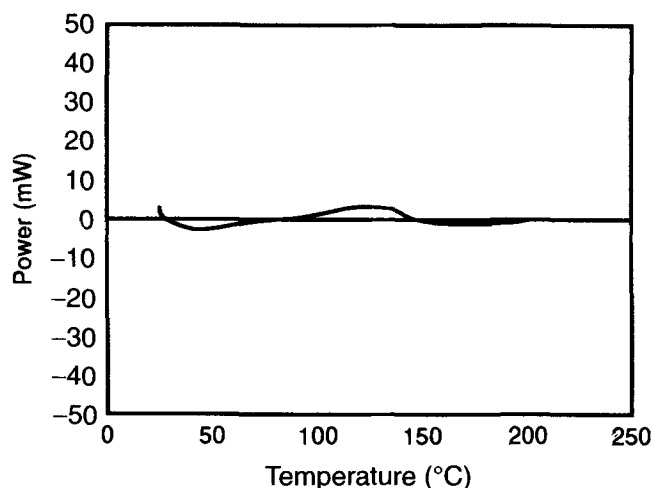


FIG. 1. Calorimetry of a C₁₂₋₁₅ (EO)₇ alcohol ethoxylate in air.

corresponding temperature increase in the sample would be less than 1°C. Again, under these conditions, there is no evidence for autocatalysis or self-heating.

Autoclave heating. Simple heating of an alcohol ethoxylate in air provides results complementary to those obtained in calorimetry. Levels of formaldehyde and acetaldehyde, both known oxidation products, increase in alcohol ethoxylate samples as a result of heating in air, but there is no evidence that alcohol ethoxylates are unstable under these conditions (Table 1). A neat sample of alcohol ethoxylate and a sample mixed 50:50 (vol/vol) with water was tested. The latter sample was used to understand whether alcohol ethoxylates are significantly more stable under heat when diluted.

As shown in Table 1, aldehyde levels in all the samples heated in the presence of quiescent air are greater than typical baseline values of around 20 ppm. Because the measurements were on the liquid sample withdrawn from the heating vessel, not on the vapor phase above the heated sample, the aldehyde levels appear to vary inversely with temperature. This apparent trend is only an artifact; as the temperature increased, aldehydes were driven into the vapor phase and were not measured. The significant observation here is not the apparent trend in aldehyde levels with temperature, but the fact that aldehydes are increased by heating.

TABLE 1
Aldehydes and Selected Ethoxamers from Alcohol Ethoxylate Samples Heated in the Presence of Quiescent Air

Sample	Temperature (°F)	HCHO (ppm)	CH ₃ CHO (ppm)	Average EO ^a	Free ROH (%wt)	EO ₂₂ (%wt)
Neat	200	215.9	74.1	7.24	1.94	0.49
Neat	300	154.6	64.9	7.26	1.88	0.53
Neat	400	78.8	59.6	7.28	1.77	0.45
50:50	200	209.4	51.3	7.23	1.91	0.43
50:50	300	110.4	51.8	7.23	1.88	0.41
50:50	400	67.4	39.9	7.23	1.90	0.34

^aEO, ethylene oxide.

An alcohol ethoxylate with an average of seven moles of ethoxylation per mole of alcohol was used in this experiment; as column five of the table shows, heating the samples brought about no significant change in the average degree of ethoxylation. Although some oxidation occurred, as indicated by the elevated aldehydes, this oxidation was not extensive enough to consume a detectable fraction of the ethoxylate chain.

The free alcohol and EO₂₂ columns of the table indicate that the left and right edges of the EO distribution were not significantly affected by heating. The free alcohol portion of the sample is the remaining unreacted alcohol after ethoxylation; EO₂₂ is the ethoxamer with the highest degree of ethoxylation detected in these samples.

Thermogravimetry. The TGA for the sample in helium is given in Figure 2. Sample mass is reduced steadily and gradually with increasing temperature up to the limit of the measurement. Approximately 65% of the sample remains on the balance pan at the end of the measurement. This weight loss profile, obtained in helium carrier gas, is typical of our findings in an inert environment. The mass spectra of components evolved is typical of hydrocarbon moieties. Because this measurement is in the presence of an inert carrier gas, the changes in sample mass are the result of simple distillation.

The TGA for a sample in air is given in Figure 3. In contrast to the results with an inert carrier gas, large mass losses are seen with increasing temperature above 150°C, up to approximately 90% at the highest temperature. Mass spectra indicate fragments at *m/z* 29, 43, and 44, suggesting acetaldehyde, and at *m/z* 45 and 60, suggesting acetic acid. For the region of sharp mass loss, the most significant peak is at *m/z* 44, shown in Figure 4. For the highest temperatures in the measurement, above 250°C, the mass spectra indicate significant hydrocarbon fragmentation.

Using the fragment at *m/z* 44 as a significant clue, we narrowed our focus to those likely oxidation products with a molecular mass of 44 Daltons—acetaldehyde and carbon dioxide. EO itself has a molecular mass of 44 Daltons, but cannot be formed under these conditions because of the large energetic cost of closing a three-membered ring; EO was not detected in our analyses.

Gas-phase sampling. Although our attempts at calorimetry in flowing air were unsuccessful, analysis of the flowing air stream for oxidation products and analysis of the residual alcohol ethoxylate sample both proved valuable. We found gradual increases in the levels of CO₂ and acetaldehyde in the vapor phase above a heated, vigorously aerated sample of C₁₂₋₁₅ 7 EO alcohol ethoxylate up to 120°C. Above 150°C, increases in both species, and in CO, are much more significant (Fig. 5). Upon heating to 120°C with air flowing through the samples at 50 mL/min, acetaldehyde detected by on-line GC in flowing air downstream from the sample increased from less than 20 ppm to approximately 200 ppm. Above 150°C, acetaldehyde levels in the vapor phase samples approached 1000 ppm. The results are similar for CO₂. Low-temperature grab samples (below 120°C) had CO₂ levels

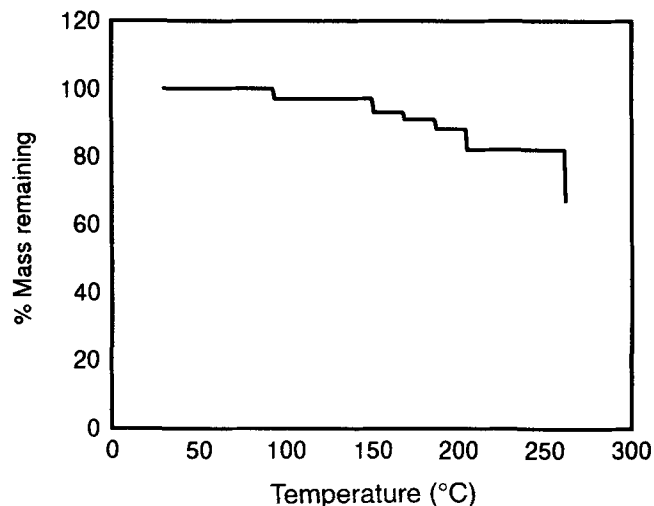


FIG. 2. Thermogravimetry of a C₁₂₋₁₅ (EO)₇ alcohol ethoxylate in flowing He.

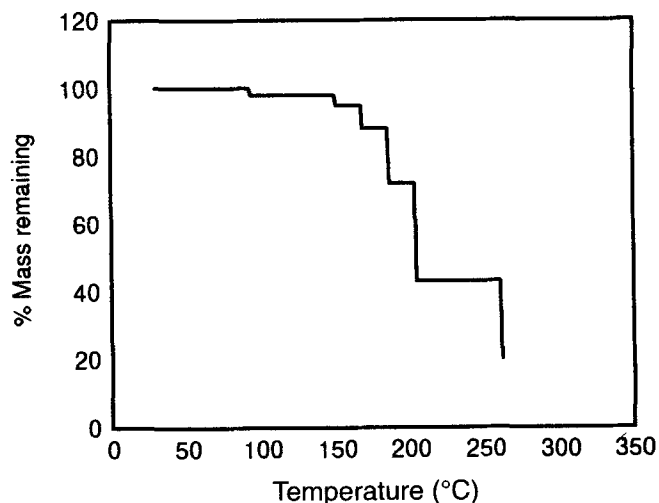


FIG. 3. Thermogravimetry of a C₁₂₋₁₅ EO₇ alcohol ethoxylate in flowing air.

ranging from about 300 to 1250 ppm. Samples drawn at higher temperatures had CO₂ levels as high as 8000 ppm at the highest temperatures. Carbon monoxide levels in grab samples behaved the same way, with no detection or relatively low levels for temperatures below 120°C and values reaching 10,000 ppm for samples drawn at temperatures from 150 to 204°C. These analytical results are not cumulative; the samples were single observations, with no attempt made to quantitate the total amount of acetaldehyde, CO, or CO₂.

Addition of an antioxidant (butylated hydroxytoluene) or adjustment of the sample pH (from 6.4 to 7.5) generally reduced the levels of acetaldehyde, CO, and CO₂ in vapor-phase samples below 150°C, but the dramatic increase above 150°C still occurred.

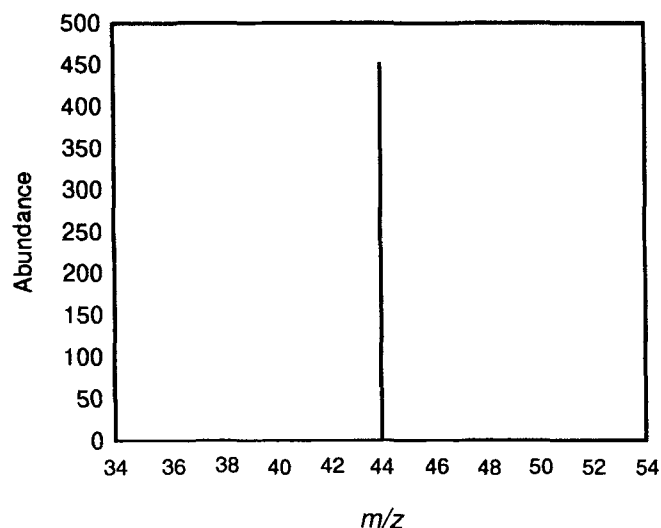


FIG. 4. Mass spectrum of volatile products in the region of sharpest mass loss during thermogravimetry in air.

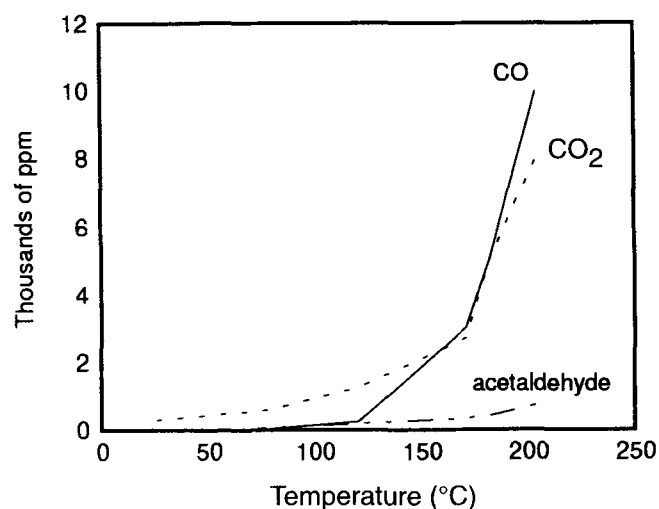


FIG. 5. Oxidation products in air after flowing through alcohol ethoxylate at 50 mL/min.

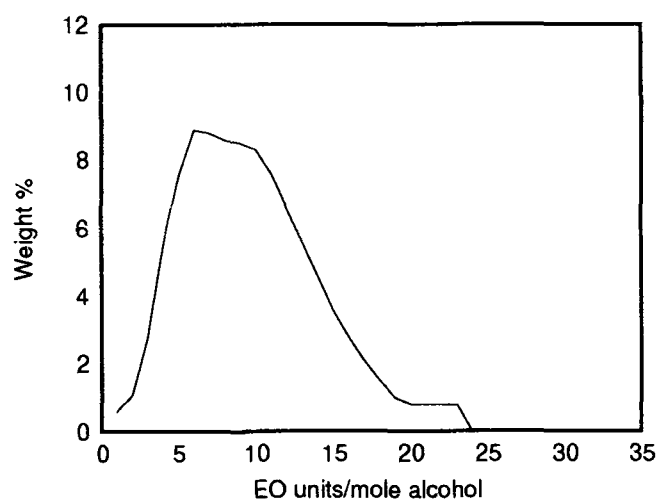


FIG. 6. Typical ethylene oxide (EO) adduct distribution for an alcohol ethoxylate with an average of 7 moles of ethylene per mole of alcohol.

Residue from the air-exposed and nitrogen-exposed samples were removed from the cells and analyzed for EOD after the heating experiments were concluded. In every case, there was discoloration of the nitrogen-exposed samples, but no significant change in EOD. For the samples exposed to flowing air, discoloration was generally much more severe, and EOD was consistently shifted to lower values, typically by about one EO unit. A typical EOD is given in Figure 6; EODs for a pair of experimental samples are given in Figure 7.

DISCUSSION

Our results indicate that a combination of heat and vigorous aeration will significantly oxidize alcohol ethoxylates. Heat alone will cause some oxidation in the presence of static air, but aeration in combination with heat will cause oxidation sufficient to reduce the degree of ethoxylation, degrading the product.

Alcohol ethoxylates are known to be stable under inert atmosphere at high temperatures. Unpublished work by J.G.F. Coolegem and J. Kars of Koninklijke/Shell Laboratory, Amsterdam, shows that a C_{14-15} alcohol with an average of 7 moles of EO per mole of alcohol is thermally stable to 300°C under a helium atmosphere. As shown in Figure 8, in the presence of helium, no thermal signal was produced when a sample was heated to 300°C over the course of five hours. The difference between T_{in} and T_{out} is inherent in the measuring technique. A driving force is required as heat is continuously applied to the reactor to maintain the temperature ramp of $1^{\circ}\text{C}/\text{min}$. The value of this driving force depends on the heat transfer characteristics of the liquid sample and will generally be a function of the temperature. Any exothermic or endothermic process will show up as a difference between T_{in} and T_{out} . The absence of such a difference indicates that no exothermic (decomposition) reactions occur over the temperature range investigated.

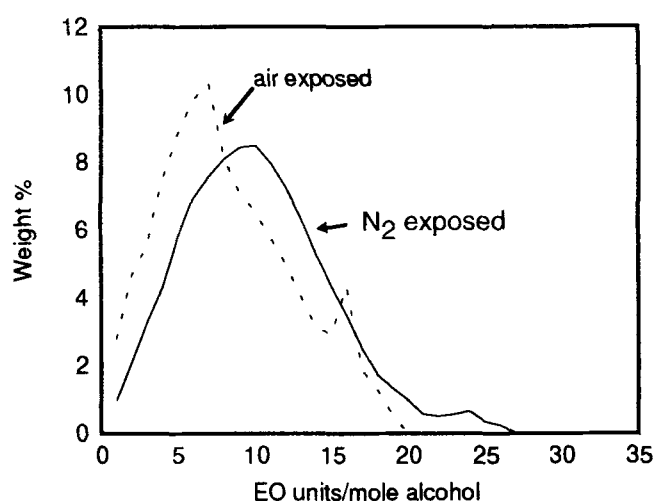


FIG. 7. Ethylene oxide adduct distribution of alcohol ethoxylate samples after exposure to flowing nitrogen and flowing air.

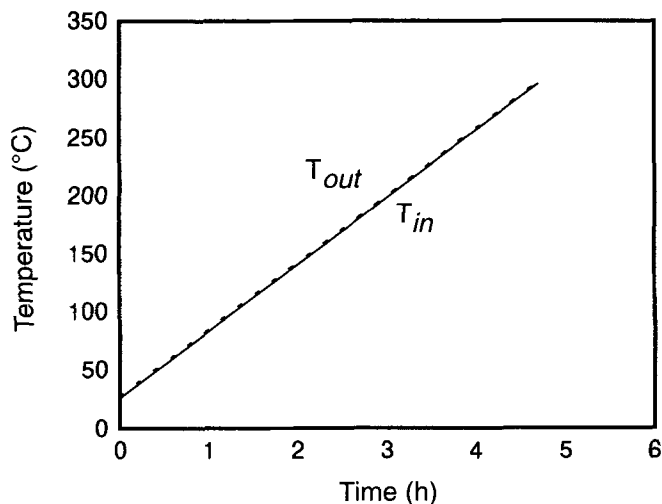


FIG. 8. Calorimetry of a C_{14-15} (EO)₇ narrow range alcohol ethoxylate in He.

In the presence of static air, heat up to 204°C will increase the levels of aldehydes in the product, indicating some oxidation; however, oxidation under these conditions is not extensive enough to reduce the degree of ethoxylation. Alcohol ethoxylates heated in this manner will be significantly discolored but will retain their chemical identity.

Our results show that alcohol ethoxylates can be oxidized, to the point of being degraded, when heated with vigorous aeration. A number of oxidation products are reported in the literature for oxidation of polyoxyethylene, including formaldehyde and formic acid (3,7), ethylene and diethylene glycol and their aldehydes, formates, and hemiformals (8,9), and acetic acid and water-soluble long-chain products (10,11). For moderate heating with vigorous aeration, with temperatures up to 120°C, acetaldehyde, carbon monoxide, and carbon dioxide are volatilized in detectable quantities. For temperatures above 150°C, all three of these species are produced in significantly higher amounts, particularly the oxides of carbon. We conclude that the chemistry of oxidation is qualitatively different for aeration at temperatures above 150°C from that for aeration at temperatures below 120°C.

The addition of a phenolic antioxidant (butylated hydroxytoluene) at 500 ppm does not change these observations. The dramatic increases in acetaldehyde, carbon monoxide, and carbon dioxide still occur for temperatures above 150°C. Phenolic antioxidants typically act as free-radical scavengers, breaking the chain reaction; under high-temperature conditions, kinetic chainlengths tend to be shorter and phenolic antioxidants routinely lose their effectiveness. Our observations are consistent with this. We see some decrease in measured acetaldehyde, CO, and CO₂ for temperatures up to 150°C, but for higher temperatures, the levels of each analyte still increase significantly.

Hamburger *et al.* (12) have reported that even small decreases in pH significantly reduce induction periods for oxidation of polyoxyethylene surfactants. We find that raising the pH of an alcohol ethoxylate from 6.4 to 7.5 has little effect on our observations. As with an antioxidant, there is a

small decrease in measured levels of CH₃CHO, CO, and CO₂ for temperatures up to 150°C, but above 150°C the large increases still occur. Here again, the effect of high temperature is a more important factor than the initial pH of the alcohol ethoxylate.

For temperatures above 150°C and vigorous aeration, oxidation of the alcohol ethoxylate is sufficient to reduce the average degree of ethoxylation. Although we measured a consistent decrease of one EO unit as a result of high-temperature, forced-air oxidation, and sampled the forced air passing out of the alcohol ethoxylate for oxidation products, we cannot relate the vapor phase levels of acetaldehyde or carbon oxides to the decrease in EO, because our vapor phase samples were drawn at infrequent intervals. The system was not closed, and no attempt was made to determine a mass balance during the forced-air oxidation.

A possible explanation for the changes observed above 150°C is the ease of air oxidation of aldehydes under these conditions. Aldehydes are routinely present in alcohol ethoxylates at levels of a few tens of ppm, and are easily oxidized by air to peracids, which decompose at elevated temperature to hydroxy and acyloxy free radicals. These radicals, in turn, can initiate oxidation of the EO chain, producing more aldehydes. We find progressively more significant oxidation on heating as we go from inert conditions to an air atmosphere to vigorous aeration, which is consistent with an aldehyde-originated oxidation. Additional studies, with careful control of the initial aldehyde levels and precise quantitation, are required to substantiate this possibility.

Alcohol ethoxylates are thermally stable at temperatures up to 300°C in an inert atmosphere. In the presence of quiescent air at temperatures up to 204°C, alcohol ethoxylates are thermally stable but will undergo sufficient oxidation to increase levels of formaldehyde and acetaldehyde to hundreds of parts per million. The EO chain of the molecule is not affected by this marginal amount of oxidation. With the combination of flowing air and heat up to 204°C, however, oxidation will occur to significantly degrade the EO chain. Acetaldehyde, carbon dioxide, and carbon monoxide are evolved and expelled into the vapor phase. For temperatures up to 120°C, levels of these species increase gradually with temperature. For temperatures above 150°C, all three species are produced in much greater amounts with increasing temperature. Carbon monoxide and carbon dioxide levels are approximately ten times higher than acetaldehyde levels in the vapor phase. The addition of butylated hydroxytoluene at 500 ppm or an increase in the alcohol ethoxylate pH from 6.4 to 7.5 will suppress the oxidation somewhat for temperatures up to 120°C, but are ineffective at suppressing oxidation at higher temperatures.

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