Mass Spectrometric Study of Nonylphenol-Ethylene Oxide Adducts

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Abstract

Individual ethylene oxide adducts of high purity have been separated chromatographically from commercial grade nonylphenoxypoly(oxyethylene)-ethanol (TERGITOL nonionic NP surfactants) and studied by time-of-flight mass spectrometric techniques. The 1–9 mole ethylene oxide adducts of nonylphenol produced clear-cut spectra with a small number of fragment ions. Four groups of different ion types have been established and some remarks concerning their formation are given. Molecular ions for the nine adducts, through mass 616, were observed in good abundances because of the low-energy and high-speed capabilities of the instrument. However, no single structure for an adduct can be proposed because the nonyl portions of the compounds are isomeric mixtures. The ionization characteristics of the NPE_n compounds reveal that the aromatic and alkyl portions of the molecules are easily activated. Tergitol nonionic NP surfactants have branched alkyl substituents and are not completely biodegradable. Therefore it is speculated that the biodegradation process leads to exposure of the highly branched alkyl-aromatic portions of the molecules in a manner comparable to mass spectral fragmentation processes.

Introduction

Mass spectrometric studies of commercial nonionic surface active agents have long been unsatisfactory because the addition of ethylene oxide to molecules containing an active hydrogen always produces complex mixtures. In particular, mass spectra obtained of nonylphenoxypoly(oxyethylene)-ethanol (Tergitol nonionic NP surfactants) are essentially meaningless because mixed spectral species from several individual compounds produced patterns which defied interpretation. The pure compounds are essential for meaningful mass spectral characterizations. Pure nonionic surfactant molecules with a common hydrophobe probably could be obtained by syntheses using the correct poly(oxyethylene) glycols. However, reactions using, for example, ethylene glycol through nonaoxyethylene glycol to produce a homologous series of pure surfactants would be prohibitive from a standpoint of time and expense.

Recently, complete separation of the individual adducts from para-nonylphenoxypoly(oxyethylene)-ethanol (NPE_n) was achieved by N. T. Crabb (1) who used column chromatographic techniques. More than 600 fractions were taken and their purity was determined by thin layer chromatography. Large numbers of fractions containing individual adducts were combined and a few milligrams of each homolog were supplied for comprehensive mass spectral investigations. A total of nine composited fractions, representing the addition of from 1–9 moles of ethylene oxide, were produced. Mass spectra of the nine nonylphenol ethylene oxide adducts (NPE_n, where $n = 1$ to 9) were obtained by use of the heated direct inlet probe of the time-of-flight mass spectrometer (TOF).

Conventional mass spectrometers have been used successfully for many years for structure correlations and the instrument has earned its position as a powerful tool for organic structure elucidations as exemplified by great numbers of publications in the recent literature. However, three distinct disadvantages impede the conventional mass spectrometer in this work. These impediments are (a) thermal energy is required to drive the sample through the inlet system, (b) the ionization chamber usually must be operated at elevated temperatures and (c) residence times of molecules and ions in the ionization chamber are long enough to permit undesirable and complicating reactions. These three conditions result in molecular decompositions, severe fragmentations, ion decompositions, ion-molecular reactions and complex rearrangement reactions which produce great numbers of primary and secondary ions. Spectra thus produced frequently may contain 100 or more individual ions and are difficult to interpret. Also, information gained from the interpretation of such complex spectra may be more significant to the understanding of instrument energetics than to chemical reaction clarification and compound categorization.

The inlet proble of the TOF permits insertion of the samples inside the ionization chamber of the TOF. The samples are held in close proximity to the ionizing electron beam (about 3 mm) and ionization is achieved with minimum time and energy. Clear and definitive mass spectra, unusual in their simplicity, are obtained. This report will discuss the fragmentation of the series of adducts and the distinct types of ions which are produced, and comment on potential correlations of biodegradability with electron-induced activations observed in the mass spectrometer.

Experimental Procedures

The mass spectrometer used in this work was a Bendix Model 14–101. (The Bendix Corporation, Scientific Instruments Division, 3625 Hauck Road, Cincinnati, Ohio 45241) which has a 1-meter flight tube and produces 10,000 complete spectra per second. During the mass spectrometric experiments, the individual adduct samples were contained in quartz glass tubes 1-mm I.D. × 10-mm long as commercially available from the Bendix Corporation. Thermal excitation of the samples was achieved by means of the heated direct insertion probe apparatus marketed by the same company. Heat was applied rapidly until a spectrum was observed on the instrument's oscilloscope-monitor and a permanent record was then secured quickly using the direct writing oscillograph attachment or a Model 2620 Polaroid camera. The temperatures at which spectra were recorded for each compound are as follows: $NPE_1 = 36$ C, $NPE_2 = 38$ C, $NPE_3 = 60$ C, $NPE_4 = 95$ C, $NPE_5 = 150$ C,

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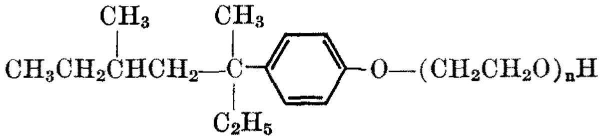
NPE_6 = 218 C, NPE_7 = 246 C, NPE_8 = 260 C and NPE_9 = 270 C.

Discussion

In the TOF instrument, each nonylphenol-ethylene oxide adduct produced a molecular ion and a series of fragment ions which can be divided into four groups of distinctly different ion types: (a) alkylphenoxylate ions (result of charge localization on the alkyl chain), (b) alkylphenoxide ions (loss of the ethoxylate chain), (c) ethoxylate chain fragment ions, and (d) typical alkyl fragment ions.

As shown in Table I, the molecular ions of the nine adducts appeared at the following mass positions: NPE_1 = 264, NPE_2 = 308, NPE_3 = 352, NPE_4 = 396, NPE_5 = 440, NPE_6 = 484, NPE_7 = 528, NPE_8 = 572 and NPE_9 = 616. These molecular ions confirmed the monoisotopic molecular weights of the individual compounds. They were produced in good abundance, in spite of their high masses, because of the low-energy and high-speed characteristics of the TOF. Conventional mass spectrometers may cause decomposition of the molecules before molecular ions can be formed, particularly when high electron beam energies are used.

Five significant fragment ions, produced by location of the positive charge at an alkyl site, were assigned to the first group listed in Table I. These ions were produced by the cleavage of an ethyl group (M-29) and additional successive cleavages of four methylene groups. The abundant ion formed by the loss of these six carbons from the alkyl chain, and the fact that no further fragmentation is observed, indicates that the alkyl chain is highly branched at the carbon adjacent to the benzene ring. Insignificant amounts of methyl ions, abundant ethyl ions, and the reluctance to produce an ion by the loss of methyl (M-15), indicates that the alkyl chain is terminated with an ethyl group. Therefore, it is proposed that many of the individual adduct molecules may exist in a structural form not commonly considered, such as the following:



It is not suggested that this structure is predominant in comparison with a large number of additional structures that can be written. The commercial product contains alkyl groups with varying configurations (2). More highly branched, or less highly branched alkyl isomers could be present, and considerable amounts of compounds similar to the above structure would produce the observed spectra.

The alkylphenoxide ions of the second group are produced by the elimination of the ethoxylate portion of the molecule by electron impact. The location of the positive charge is then on the phenol oxygen atom (the heteroatom), a favored site for charge localization. The rather short length of the alkyl portions of these ions (one to five carbons) illustrates the branched configuration of the hydrophobe portion of the surfactant.

The ions of the ethoxylate portion (third group of Table I) of each molecule of the NPE series are well defined. The terminal ethoxy group (C_2H_5O +, mass 45) is the favored ionic species for each adduct. Diminishing abundances of larger ethoxy combinations are expected, and when n = 4 in the $(C_2H_4O)_nH$ chain, the inherent instability of the large group prevents the retention of the positive charge without fragmentation.

The alkyl ions of the fourth group appear in a rather conventional order. The abundance of the C-3 ion suggests that propyl groups can be produced in good abundance. Ethyl (C-2) and butyl (C-4) ions are formed easily, and pentyl (C-5) ions are present in good abundances. The hexyl (C-6) ions are of significant abundances, but the absence of larger alkyl groups substantiates the highly branched state of the nonyl portion of the molecules.

Because the nonyl portions of the adducts are

TABLE I

Mass Spectra of Ethylene Oxide Adducts of Nonyl Phenol

Ion	Mass	Rating of Ion Abundance[a]								
		1-Mol Mass 264	2-Mol Mass 308	3-Mol Mass 352	4-Mol Mass 396	5-Mol Mass 440	6-Mol Mass 484	7-Mol Mass 528	8-Mol Mass 572	9-Mol Mass 616
Alkylphenoxylate										
$C_9Ph(EtO)_n$	M	**	**	**	**	**	**	**	**	**
$C_7Ph(EtO)_n$	M-29	*	*	*	*	*	*	*	*	*
$C_6Ph(EtO)_n$	M-43	*	*	*	*	*	*	*	*	*
$C_5Ph(EtO)_n$	M-57	*	**	*	*	**	*	**	**	*
$C_4Ph(EtO)_n$	M-71	***	***	***	***	***	***	***	***	**
$C_3Ph(EtO)_n$	M-85	****	****	****	****	****	****	****	****	****
Alkylphenoxide										
C_5PhOH	163	....	....	....	....	....	....	*	*	*
C_4PhOH	149	*	*	*	*	*	*	*	*	*
C_3PhOH	135	**	****	****	****	****	****	****	****	****
C_2PhOH	121	***	**	**	**	**	**	**	**	**
CH_2PhOH	107	****	***	***	**	***	**	*	*	*
CH_2Ph	91	*	*	*	***	***	***	***	***	***
Ph	77	*	*	*	*	*	*	*	*	*
Ethoxylate										
$(EtO)_4$	177	....	....	....	*	*	*	*	*	*
$(EtO)_3$	133	....	....	*	**	**	**	**	**	*
$(EtO)_2$	89	....	*	**	**	***	****	****	****	***
EtO	45	******	******	******	******	******	******	******	******	******
Alkyl										
C-6	85	*	*	*	*	*	*	*	*	*
C-5	71	*	*	*	**	**	**	**	**	**
C-4	57	**	**	**	***	***	**	**	**	**
C-3	43	****	****	****	****	****	****	****	****	****
C-2	29	***	***	***	**	**	***	***	**	**

[a] Number of asterisks indicate relative abundance.

isomeric mixtures, no single structure for an adduct can be proposed. However, the molecular weights of the individual adducts were verified. In addition, the ionization characteristics of the NPE_n compounds reveal that the aromatic and alkyl portions of the molecules are easily activated. This may be indicative of the lack of aerobic biodegradability exhibited by Tergitol nonionic NP surfactants (3). Branched alkyl substituents commonly discourage biodegradability (4,5). It is interesting to speculate that the aerobic degradation process would lead to exposure of the highly branched alkyl-aromatic portions of the molecules in a manner similar to the electron-induced activation witnessed in the mass spectrometer.

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