Gas-Liquid Chromatographic Separation of Ethylene Oxide Adducts of Fatty Alcohols Via Their Acetate Esters[1]

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Abstract

Gas-liquid chromatography (GLC) of ethylene oxide adducts of fatty alcohols is carried out after conversion of the alcohols to acetate esters. This conversion permits detection of higher mol wt compounds. Separate peaks for adducts with up to 13 units of ethylene oxide are obtained for a product derived from dodecyl alcohol. The procedure is used to follow the course of a molecular distillation of an adduct prepared from hexadecyl alcohol and an example is also shown for an adduct derived from a mixture of dodecyl and tetradecyl alcohols.

Introduction

SURFACE ACTIVE AGENTS derived from the addition of ethylene oxide to alcohols or phenols have long represented the major share of the nonionic class of products. Until recently the most important members of this class have been adducts of alkylphenols. The usual process involves the addition of a small amt of alkali catalyst to the phenol prior to the addition of ethylene oxide. The reacting species is initially the phenylate anion and, later, the anion of the ether-alcohol adduct. Inasmuch as the phenol contains the more acidic proton, the first mole of ethylene oxide reacts almost entirely to produce ethylene glycol mono-ether. Subsequent addition of ethylene oxide occurs largely at random to produce a mixture of varying chain length which has been shown to have a mol wt distribution close to that calculated for a Poisson distribution (4).

In the case of the alkali-catalyzed reaction of a fatty alcohol, the rate of reaction of the ether-alcohol adducts with additional ethylene oxide is greater than that of the starting alcohol (3,5). This results in a broader distribution of chain lengths than predicted for a Poisson distribution. Tischbirek (8) and Stockburger and Brander (7) also have shown that the use of acid catalysts may substantially increase the rate of reaction of the parent alcohol relative to the ether-alcohol adducts.

One of the earliest analytical studies of the chain-length distribution of an ethylene oxide adduct using distillation techniques was by Mayhew and Hyatt (4) based on the determination of hydroxyl numbers of successive fractions from a molecular distillation of a nonylphenol ethylene oxide adduct. Other approaches have involved liquid-phase chromatography. Kelly and Greenwald (3) described a separation of fractions of different chainlength in the chromatography of an octylphenol adduct on silicic acid. Improved resolution for the lower members of a series of dodecyl alcohol adducts was obtained by Puthoff and Benedict. These authors converted the nonionic mixture to a mixture of p-phenylazobenzoyl esters which they chromatographed on alumina. In the same article they also referred to a gas chromatographic method using a 6-ft column of Apiezon L on Chromasorb at 240C. Although they were successful in a quantitative analysis of the first two ethenoxy adducts, they re-

ported excessive retention times and incomplete elution from the column for higher members of the series.

Experimental

Apparatus. An F&M Model 500 chromatographic instrument with temp-programming and a thermal conductivity detector was used in this work.

Column. A stainless steel column, 2 ft long and 0.25 in. diam, was packed with 2% silicone gum rubber (GE SE-30) on 30–60 mesh acid-washed "Chromasorb W." The column was initially conditioned by attaching only the inlet side and holding the oven temp at 450C for 15 min with no flow of helium. The temp was then reduced to 400C for one hr while maintaining a 100 ml/min flow of helium through the column.

Operating Conditions. The injection port temp was normally maintained at 425C and the detector block was at 418C. The latter temp was lowered to 350° when not in daily use in order to prolong the life of the detector. The column temp was programmed from an initial value of 125C to a maximum of 405C at heating rates varying from 5.6–15 degrees/min. A flow of helium was maintained at ca. 100 ml/min.

Conversion of Alcohols to Acetate Esters. A small cylindrical reactor, 2 cm diam and 20 cm high, was equipped with a capillary inlet for nitrogen at the bottom, a thermocouple well, a reflux condenser and a vacuum outlet. A few tenths of a gram of sample were introduced along with 100 mole % excess acetic anhydride and refluxed for 15 min. By-product acetic acid and most of the excess acetic anhydride was then
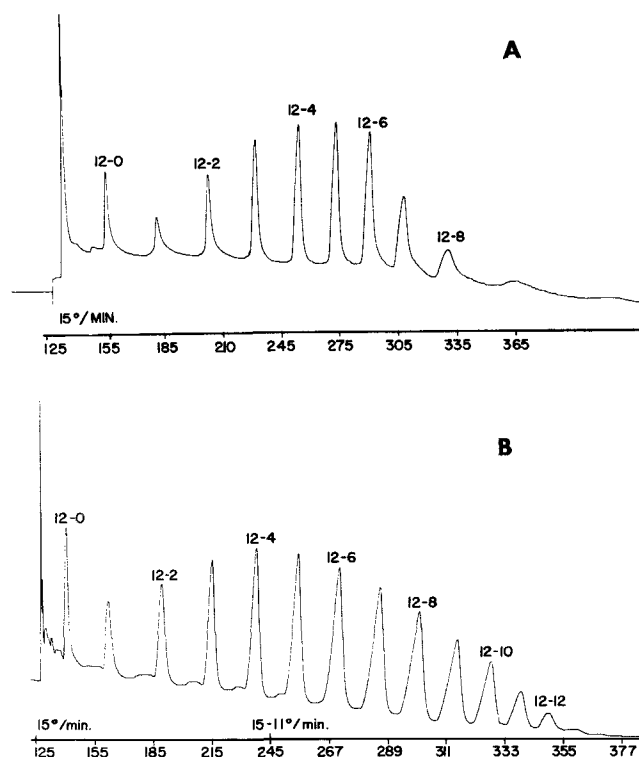

FIG. 1. a) Dodecanol + 6 E.O. adduct before acetylation; b) after acetylation.
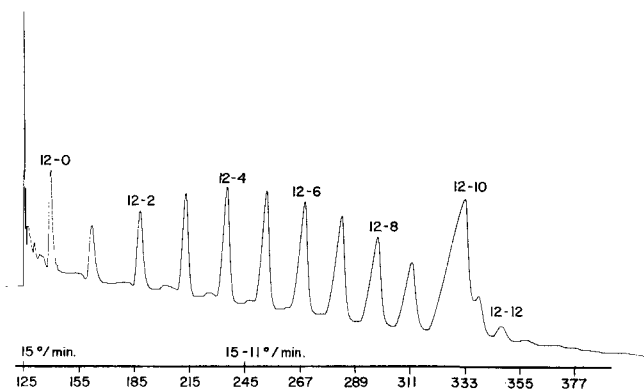
FIG. 2. Dodecanol + 6 E.O. adduct with addition of pure 12–10 adduct.

removed under reduced pressure(down to one mm at 100C).

Monododecyl Ether of Decaoxyethyleneglycol. Following a procedure similar to that of Fordyce, Lovell and Hibbert (1), decaoxyethyleneglycol was prepared by the addition of β-chloroethyl ether to the sodium salt of tetraoxyethyleneglycol in an excess of the free glycol which had been fractionated in a spinning band column from "Carbowax 200." The crude reaction product was filtered free of salt and molecularly distilled in a "Rotafilm" still (Arthur F. Smith, Inc.). A fraction distilling at a wall temp of 175C at 1μ pressure was collected and found to be a single component by GLC, and had an IR spectrum similar to that of a commercial sample of polyoxyethyleneglycol (Carbowax 400). The purified glycol was used to prepare the monoether by a procedure similar to that of Gingras and Bayley (2).

To 38.2 g of the decaoxyethyleneglycol (1/12 mole) was added 1/15 mole sodium methylate as a 25% solution in methanol. Methanol was removed under reduced pressure and then 16.6 g of dodecyl bromide (1/15 mole) was added with stirring at 130C over a half hour period. Stirring was continued at this temp for an additional hr. The reaction mixture was allowed to cool and filtered free of salt through a fritted glass disc in a suction flask. The crude filtrate, 49.4 g, was dissolved in 200 ml 50% aqueous methanol and extracted with 300 ml of hexane. From the resultant hexane layer we recovered 9.1 g of crystals, mp 35–39C, which we believe to be the didodecyl ether of the glycol. The lower layer from the hexane extraction
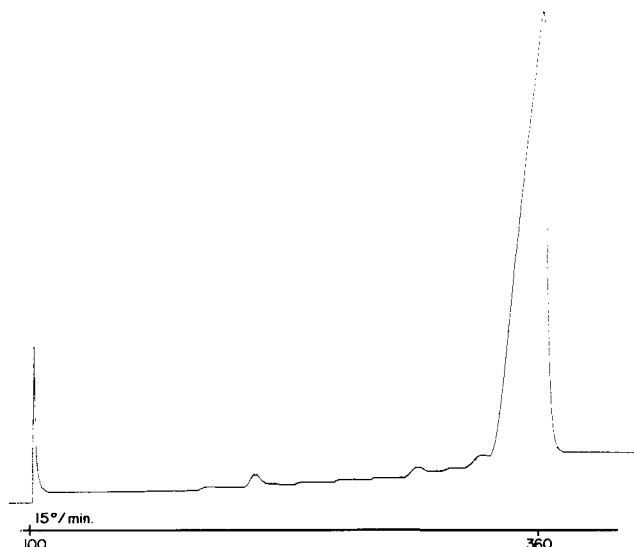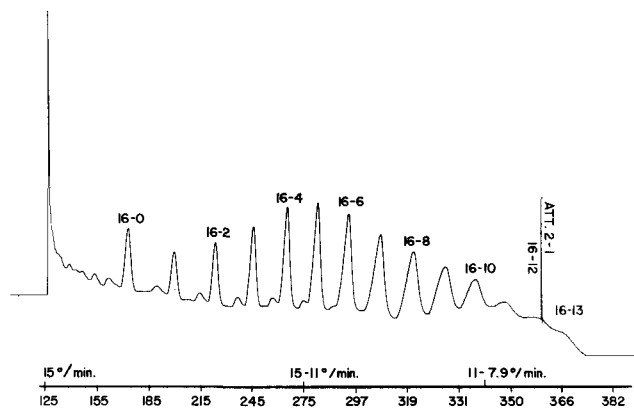
was extracted with 300 ml ethyl ether. The oily residue recovered from the upper layer after drying over sodium sulfate and evaporation of excess ether was molecularly distilled to yield a solid fraction which distilled at 220C wall temp at 1 μ pressure. Successive recrystallizations from hexane and ether yielded 4.1 g of the monododecyl ether of decaoxyethylene glycol, melting at 35.6–36.5C. After conversion of this material to its acetate ester, the chromatogram in Figure 3 was obtained.

Ethylene Oxide Adducts of Fatty Alcohols. The addition of ethylene oxide to fatty alcohols was carried out in the general manner described by Satkowski and Hsu (6) with 0.036 moles potassium hydroxide/mole of alcohol and a reaction temp of 130–140C.

Molecular Distillation of Hexadecanol Adduct. The "Rotafilm" still was used to fractionate an ethylene oxide adduct of hexadecanol. The nonionic was fractionated at a pressure of one μ or less and successive fractions of distillate were obtained by increasing the temp of the distilling surface by 25° intervals for each pass of the residual liquid as measured by a thremocouple inside the heating jacket.

Discussion

GLC appeared to offer the best means of obtaining a rapid estimate of the chain length distribution of an ethylene oxide adduct. The main problems encountered were excessive retention times at the usual temp ranges and the apparent decomposition which occurred at higher temp. By converting the primary hydroxyl group of a nonionic agent to an acetate ester group, the stability of the molecule to high temp gas

FIG. 4. Hexadecanol + 8 E.O. before molecular distillation.
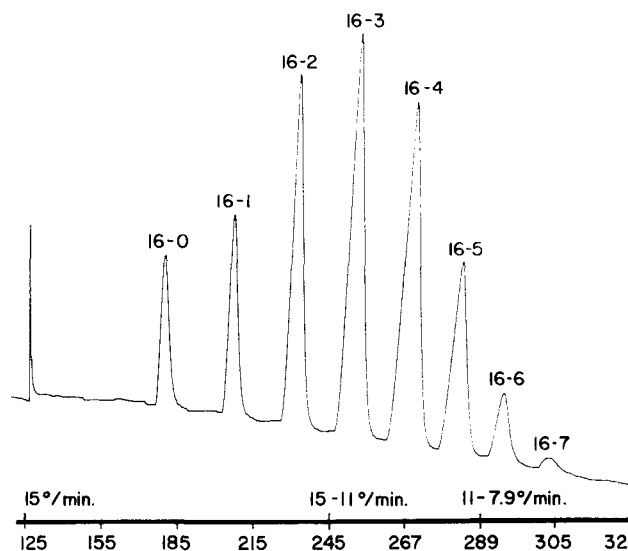

FIG. 3. Purified 12–10 adduct.

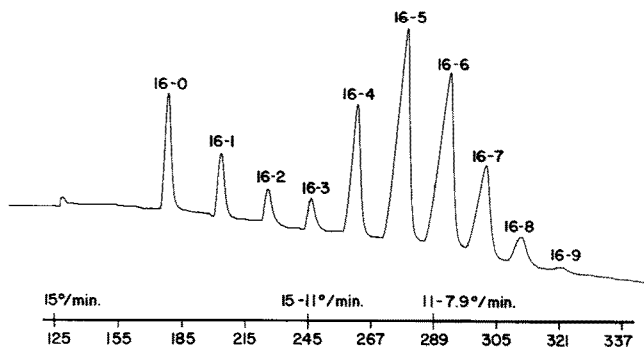FIG. 5. 150° cut of hexadecanol adduct.

FIG. 6. 175° cut of hexadecanol adduct.

chromatography is apparently greatly increased. This is illustrated in Figure 1 which compares the results obtained when an ethylene oxide adduct of dodecyl alcohol was chromatographed before and after conversion to an acetate ester. Figure 1a shows the unacetylated sample with an initial large peak of unreacted dodecanol and subsequent peaks containing one or more ethenoxy units as indicated by the number code (e.g. dodecanol with 4 ethenoxy units is 12-4). Note that the last two peaks containing 7 and 8 ethenoxy units are much reduced in area and that no peaks beyond 12-8 are apparent. Figure 1b shows that in addition to the initial peak of dodecyl acetate there are 13 peaks representing adducts with from 1–13 ethenoxy units added. A comparison of figures 1a and 1b does not accurately reflect the comparative retention times of the free alcohols vs. the acetate esters since these runs were made at different flow rates. In general the retention times of the acetate esters are somewhat longer than the corresponding alcohols.

Positive identification of peaks was possible in several cases where we had available samples containing a single chain length of ethenoxy units. Figure 2 shows the results obtained when some of the purified monododecyl ether of decaoxyethyleneglycol was added to the original sample of the six-mole adduct of dodecanol before acetylation.

Gas chromatography was also useful in characterizing the purity of preparations of homogeneous chain length. In Figure 3, the acetylated 12-10 compound shows only traces of impurity after a final recrystallization.

The technique was also useful in following the distribution of chainlength in fractions obtained by molecular distillation. Figure 4 shows the chromatogram of an acetylated sample of hexadecyl alcohol to which 8.3 moles of ethylene oxide had been added/mole of starting alcohol. Figures 5,6 and 7 are chromatograms of the first three distillate fractions obtained at wall temp of 150, 175 and 200C. In comparing the initial 150° fraction with the 175° frac-
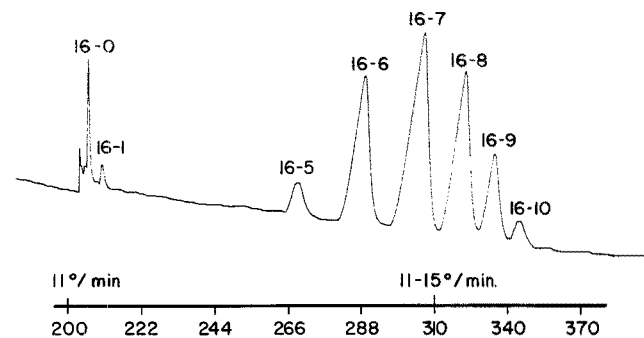

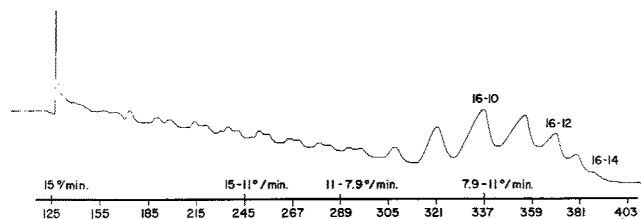FIG. 7. 200° cut of hexadecanol adduct.

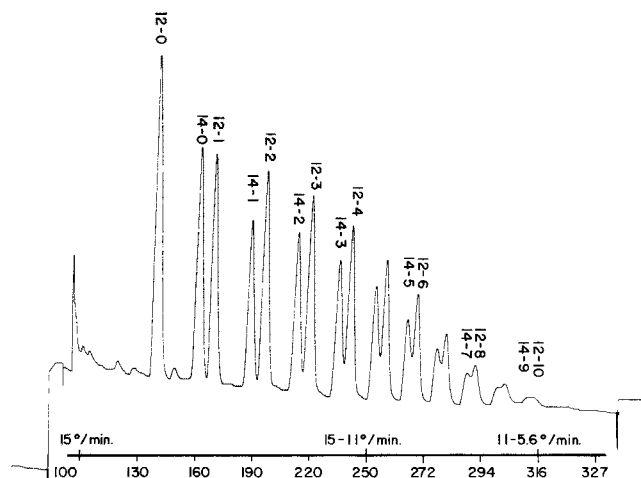FIG. 8. 275° cut of hexadecanol adduct.

FIG. 9. Mixture of dodecanol and tetradecanol + 3 E.O.

tion, there is a relatively greater amt of unreacted hexadecanol in the second fraction than in the first. The 200° fraction still contains small amt of the 16-0 and 16-1 compounds although the intermediate 16-2, 16-3 and 16-4 compounds have been completely removed in earlier fractions. We believe this illustrates an essential difference between distillation in which the composition of the distillate is determined by the partial pressures of the components and molecular distillation in which the relative rate of evaporation from the liquid surface is the determining factor.

For fractions collected up to 250C wall temp, there is no evidence of decomposition as indicated by a flat base line prior to the appearance of known components of the original mixture. However in a final fraction obtained at 275C, Figure 8, there is evidence of some decomposition as indicated by the appearance of numerous new small peaks prior to those expected from the original sample.

Figure 9 shows the results obtained from a mixture of dodecanol and tetradecanol with 3 moles ethylene oxide added/mole of original alcohol. Following the initial peak of dodecanol the subsequent pairs of peaks have been identified as a tetrodecyl derivative followed in each case by the next member of the dodecyl series.

In other runs, relative peak areas appeared to be greatly dependent upon factors such as flow rate, heating rate and temp of the injection part. Different columns also produced changes in relative peak areas. We hope that further work will uncover more reproducible conditions in order that a quantitative procedure may be developed.

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