stepwise processes in which all bromine atoms of the polybromides are not eliminated.

Apparently stearolic acid cannot be reduced by sodium in liquid ammonia possibly because of its low solubility. The liberation of stearolic acid from dibromo-oleic acid confirmed this idea. The other acetylenic compounds have been reduced by sodium in liquid ammonia (7). Furthermore the fact that 3,4-dibromohexene and 3, hexyne both yield *trans,* 3-hexene, gives some clues to the steps in the sodium debromination and reduction in liquid ammonia. The 1,2-dibromo ethylene structure is debrominated with sodium in liquid ammonia to the acetylenic bond, which immediately is reduced by the sodium and liquid ammonia to the ethylenic bond. The insolubility of stearolic acid in liquid ammonia possibly prevents the reduction processes which proceed smoothly in the cases of 3, hexyne and its derivative. However, if the electron addition to the triple bond and the subsequent repulsion of alkyl groups are necessary for reduction of the triple bond as postulated by Greenlee and Fernelius (11), either electron addition will not be possible because of the insolubility mentioned, or the repulsion processes cannot occur in the long chain alkyl groups.

Summary

1. 9,10-Dibromostearic acid has been prepared in different grades of purity through urea-inclusion compounds from natural sources of fatty acids. This facilitated preparation of stearolic acid.

2. The degree of separation of stearolic acid from other fatty acids and polymers by means of urea-inclusion compounds was ascertained.

3. The attempts at preparation of behenolic acid by dehydrobromination of 13,14-dibromobehenic acid ended in failure.

4. Stearolic acid could not be reduced by sodium in liquid ammonia. Debromination of 9,10-dibromo-oleic acid yielded stearolic acid whereas reduction of 3, hexyne and debromination of 3,4-dibromohexene resulted in the formation of *trans,* 3-hexene. Hence a reaction sequence involving debromination of vinylic dibromides and subsequent reductive hydrogenation has been proposed.

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Direct Potentiometric Titration of Oxirane Oxygen by Hydrogen Chloride-Acetic Acid[1]

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WITH THE ADVENT OF epoxy plasticizers, epoxy resins, and the use of epoxy compounds as intermediates and reagents a variety of methods have been developed for the determination of oxirane oxygen. All of these methods are indirect and can be classified under the following groups:

a) hydrochlorination in ethers, pyridine, water, or alcohols (2, 4, 7, 9, 11).
b) reaction with amines (6, 5, 8).
c) hydration of epoxy groups (8).
d) reaction with sodium sulfite, sodium thiosulfate, alkali derivatives of thiols, hydrogen sulfide, and alkali hydrosulfides (3, 10, 12).
e) reaction with anilinium hydrochloride in glacial acetic acid and back titration of the liberated aniline (1).

The methods that have found the widest applicability are those employing hydrochlorination in ethyl ether (9), pyridine (2), or dioxane (7). The long reaction time (3 hrs.) and the inconsistency of results obtained by the ethyl ether-hydrochloric acid method, especially during the summer months, are well known. The special purification of dioxane required and the weak end-point make the dioxane hydrochloric acid method time-consuming and unreliable. The pyridine hydrochloride reagent requires a carefully controlled reflux reaction time. The odor of pyridine makes its use for routine analysis objectionable.

The present method[2] was developed in order to overcome the difficulties of the existing methods and to provide a method which is more consistent, reliable, accurate, and direct.

The acetic acid-hydrochloric acid method is based on the fact that compounds which exhibit weak basic properties in aqueous solutions can be titrated readily in glacial acetic acid. Acetic acid is an acidic solvent and a poor proton acceptor. Therefore only those substances which are the strong acids in water, such as perchloric, sulfuric, hydrobromic, and hydrochloric acids, exhibit marked acidic character in acetic acid. Preliminary investigations indicated that perchloric acid and sulfuric acid gave side reactions when employed for titration of epoxy compounds in glacial acetic acid. Hydrochloric acid and hydrobromic acid were acceptable. The present paper deals with the titration of oxirane oxygen by hydrochloric acid-acetic acid. A subsequent paper will detail work done with a hydrobromic acid-acetic acid reagent.

Experimental

A. Reagents and Apparatus

1. A Beckman pH meter Model H-2 with a capillary calomel electrode and a glass electrode, red label 8990-80.
2. Reservoir Buret Karl Fisher type with long-angled tip and

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[1] Paper presented at the 29th Fall Meeting of the American Oil Chemists' Society, Philadelphia, Pa., Oct. 10, 1955.

[2] The possibility of using hydrogen chloride in glacial acetic acid was first suggested by V. C. Mehlenbacher of Swift and Company at a meeting of the A.O.C.S. Oxirane Oxygen Analytical subcommittee. Work in Swift laboratories, using indicators, had given poor endpoints and erratic results.

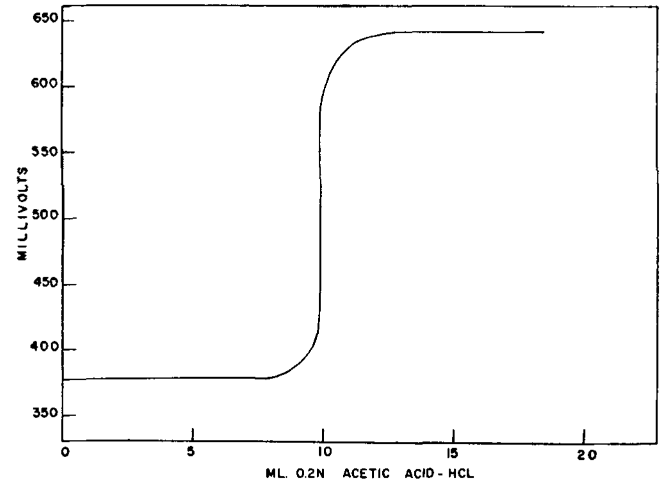

FIG. 1. Potentiometric Titration of Butyl Epoxy Stearate.

automatic zero adjustment (complete buret assembly obtainable from Arthur H. Thomas Company, Philadelphia 5, Pa., Catalog No. 2484-B).

3. A three-way bridge tube of a diameter of 10 mm. with medium porosity fritted disc insertions at the ends, bridging a distance of 50 mm. The upper arm of the salt bridge tube is tooled to accommodate a No. 1 rubber stopper.
4. A large test tube 100 x 38 mm. fitted with a No. 9 rubber stopper with two openings to accommodate one arm of the salt bridge tube and the calomel electrode.
5. 0.2 N glacial acetic acid—HCl, prepared by bubbling anhydrous hydrogen chloride through glacial acetic acid. The solution is standardized against primary standard sodium carbonate dried in an oven at 120°C.
6. Saturated lithium chloride-acetic acid solution, prepared by dissolving 0.5 g. of gelatin in hot glacial acetic acid and adding an excess of lithium chloride. This solution is used to fill the salt bridge.
7. Saturated potassium chloride in distilled water used to fill the test tube.

B. Procedure

Dissolve 0.5 to 1.0 g. of the sample to be analyzed in 20 ml. of glacial acetic acid in a 50-ml. lipless beaker. After solution of the sample, lower the electrode assembly indicated in Figure II so that one end of the bridge and the glass electrode are in the acetic acid solution 5 mm. above the stirring rod. Place the tip of the buret 1 cm. above the acetic acid solution. Add the titrant in 2- to 3-ml. increments at the beginning of the titration and then decrease to smaller increments as the end-point approaches, indicated by the drifting galvanometer needle or alternately by a change in color (from violet to blue green) when 4 drops of 0.1% crystal violet is added to the solution being titrated. The end-point is detected by the galvanometer needle, indicating a maximum deflection or by plotting the voltage as in Figure 1. The millivolt scale of the potentiometer is used in these titrations. A typical titration curve is given in Figure 1. The reaction rate of the titrant with the epoxy compounds being titrated is nearly instantaneous with all compounds examined and decreased in rate as impurities are increased. Calculate the percentage of oxirane oxygen as follows:

$$\% \text{ of oxirane oxygen} = \frac{\text{ml. titration x normality x 1.6}}{\text{weight of sample}}$$

The results obtained by this method were compared by those obtained by the ether-hydrochloric acid method of Swern, Findley, Brelen, and Scanlan (11) (see Table I).

TABLE I

Comparison of Oxirane Oxygen Determinations by the Acetic Acid-HCl and Ether-HCl Methods

Compound	% of Oxirane Oxygen	
	Acetic Acid-HCl[a]	Ether-HCl[a]
9,10-Epoxystearic Acid	5.34	5.33
9,10-Epoxyoctadecanol-1	5.61	5.62
Methyl Epoxystearate	5.12	5.12
Butyl Epoxystearate	4.49	4.50
Epoxy Soybean Oil	6.50	6.50
Dodecene Oxide	8.66	8.63
Caprylene Oxide	12.50	12.51
Cyclohexene Oxide	16.26	16.24
Glycidyl Phenyl Ether	10.58	10.54
Glycidyl Allyl Ether	14.01	14.00

[a] All these results are the mean value at least three determinations.

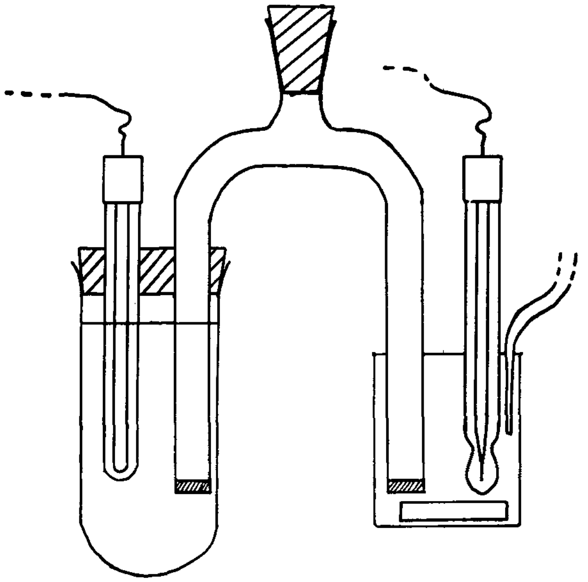

FIG. 2. Titration Cell and Salt Bridge Assembly.

Discussion

The above method was applied to a series of purified epoxy chemicals and epoxy plasticizers. The results are shown in Table I. The method is applicable to a great variety of epoxy compounds. The results are highly consistent and in agreement with the ether-hydrochloric acid method. Since compounds having acidic ionization constants of approximately 10^{-5} in water are neutral in glacial acetic acid, carboxyl groups do not interfere with the titration. The acid correction and the errors introduced by the three separate titrations in the ether-hydrochloric acid, pyridinium chloride-pyridine, and dioxane-hydrochloric acid methods are eliminated. Acetic acid with its rather low dielectric constant is a very good solvent for covalent substances. Epoxy compounds are readily dissolved. To avoid possible ring opening the epoxy compounds to be analyzed are dissolved in glacial acetic acid immediately prior to titration. Daily standardization of the reagent is necessary.

Summary

A new direct potentiometric titration method for the determination of oxirane oxygen has been developed. This method is applicable to a great variety of epoxy compounds and epoxy plasticizers. Carboxyl groups do not interfere, and a greater accuracy and reproducibility are obtained than in any of the indirect methods used.

Acknowledgment

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Fractionation of Some Polyethenoxy Lauryl Ethers

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WHEN ETHYLENE OXIDE is condensed with a fatty acid, alcohol, or alkylphenol to form polyethenoxy nonionic detergents, the average number of ethenoxy groups can usually be determined from the weights of starting materials or, in the case of the ester-type products, from saponification equivalents (1). It would be of interest to determine the exact composition and the distribution of ethenoxy groups in various ethenoxy substituted ethers or esters. The present paper deals with the molecular distillation of ether-based nonionic detergents prepared from lauryl alcohol and analysis of the various fractions to obtain such a distribution curve. In addition, detergency data are presented for the individual fractions illustrating the effect of ethenoxy substitution on soil removal and whiteness retention.

The nonionics reported herein were chosen in such a manner that the hydrophobic group would be a single substance rather than a mixture of isomers, and the molecular weight of the hydrophobe and hence of the nonionic was kept rather low in order to avoid decomposition. Distribution curves for the polyethylene glycols have been calculated by Flory (2) according to Poisson's Law, and experimental results obtained by molecular distillation of polyethylene glycol (3) support the theory.

Preparation of the Polyethenoxy Ethers

Lauryl alcohol (m.p. 21–22°C.) was condensed with ethylene oxide, using 0.5% by weight of potassium hydroxide catalyst according to directions previously described (4). The refractive index and composition of the products chosen for molecular distillation are recorded below.

Polyethenoxy lauryl ether A (6.88 ethenoxy units) was prepared by condensing 163 g. of ethylene oxide with 100 g. of the alcohol while B (9.90 ethenoxy units) was made from 234 g. of ethylene oxide and 100 g. of lauryl alcohol. A and B gave refractive indices (N_D^{25}) of 1.4564 and 1.4580, respectively.

Prior to distillation 100 ml. of the nonionic ether were treated with the exact amount of concentrated hydrochloric acid required to neutralize the potassium hydroxide used in the condensation.

Molecular Distillation and Analysis

One hundred ml. of each of the polyethenoxy lauryl ethers were carefully fractionated at approximately 0.02 mm., using a short-path type distillation apparatus, into 3 ml. fractions, each of which was analyzed by a carbon determination as well as by refractive index. Figure 1 illustrates the change in ethenoxy units of the lauryl ether with carbon content as well as with refractive index. The latter values were obtained by preparing a variety of lauryl ethers with a known average number of ethenoxy groups and measuring the refractive index of each composite sample. It was later found that refractive index values could be correlated fairly well with the carbon determinations on the individual distilled samples.

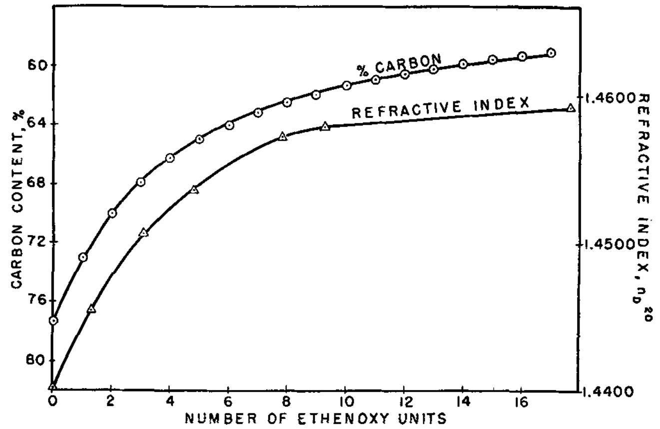

FIG. 1. Variation in carbon content and refractive index with ethenoxy chain length of polyethenoxy lauryl ethers.

After distillation a curve was plotted for variation

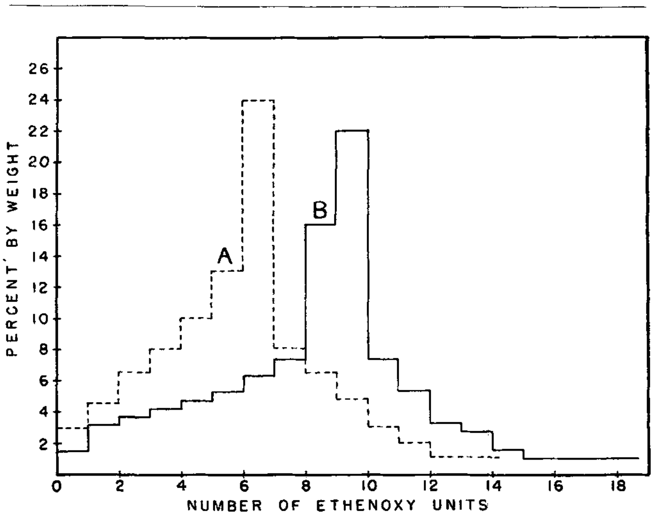

FIG. 2. Distribution of polyethenoxy lauryl ethers in terms of weight proportion at each ethenoxy level. (A = 6.88 and and B = 9.90 ethenoxy units.)