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a particular distribution curve is approximated by the exponential function, Equation 3. One source of error is the symmetry of the exponential function. A perfectly symmetrical distribution results only when the fraction in the stationary or moving phase is 0.5 ($K = 1$). The error from this source decreases both with approach to this condition and with increasing n. If n calculated for $t = 1$ was in error by Δn, then the error in n for some larger value of t would be $t^2\Delta n$. However, t varies only from 1 to 3.27 for fractions between nX and r_i of 0.3413 and 0.4995, respectively.

In all the preceding, it has been assumed that the solutes behave ideally and that the volumes of the moving and stationary phases are equal.

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Direct Titration of Oxirane Oxygen with Hydrogen Bromide in Acetic Acid

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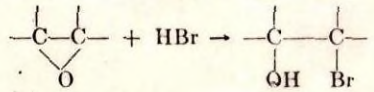
A direct method for titrating oxirane oxygen with hydrogen bromide in acetic acid makes possible the determination of a variety of epoxy compounds, epoxy resins, and epoxy plasticizers with increased speed and accuracy. Carboxylic acids, aldehydes, ethers, esters, and peroxides do not interfere. Hydroperoxides react slowly with the reagent but give no interference.

EPOXY compounds have assumed commercial importance in recent years with the advent of resins, epoxy plasticizers, epoxy stabilizers, and epoxy insecticides. This has focused increased attention on analytical methods for oxirane oxygen. Until now oxirane oxygen has been determined by indirect methods (*1-3, 5, 6, 8, 9, 11*). The methods that have found the widest applicability because of their specificity employ hydrogen chloride in ether, dioxane, and pyridine (*2, 6, 9, 11*). All these methods are based on the addition of hydrogen chloride to oxirane oxygen to form the corresponding chlorohydrin. The difference between the amount of unconsumed hydrochloric acid and that of the corresponding blank is a measure of the epoxy content. As carboxylic acids interfere with these determinations, a correction for the amount of acid present in the sample has to be made. In general, these methods require appreciably more time and operations and involve errors of three, as compared with one, separate titrations to obtain the oxirane oxygen content.

The first direct titration procedure for oxirane oxygen (*4*) employed an acetic acid–hydrochloric acid reagent. Titrations were performed potentiometrically. The method presented here is an improved and simplified procedure, which utilizes an acetic acid–hydrobromic acid reagent. Visual end points can be employed and the general range of applicability is considerably extended. Hydrogen bromide is a much stronger acid than hydrogen chloride in glacial acetic acid (*7*) and reacts to a faster rate with the α-epoxy group.



REAGENTS

Acetic acid, glacial, analytical reagent grade.
Benzene, analytical reagent grade.
Chlorobenzene, Eastman Kodak Co.
Crystal violet indicator solution, 0.1% crystal violet (Eastman) in glacial acetic acid.
Hydrogen bromide, anhydrous, Matheson Co.
Hydrogen Bromide in Acetic Acid, 0.1N. Bubble anhydrous hydrogen bromide at a slow rate through 1 liter of glacial acetic acid, until the desired normality is attained. Standardize against 0.1 gram of sodium carbonate, dissolved in 5 ml. of glacial acetic acid, and titrate to the blue-green end point of the crystal violet indicator.
Sodium carbonate, primary standard grade, Mallinckrodt. Dry to constant weight at 120° C.

APPARATUS

Reservoir Buret, Karl Fischer Type, Arthur H. Thomas Co., No. 2484-B. Fill the drying tubes of the reservoir and buret with Todd universal absorbent. Replace the drying tube of the reservoir with a ball joint stopper when the buret is not in use.
Rubber Stopper, made of soft red rubber with section perforated to within 1 mm. of the top (Will Corp., No. 6402). Make a spherical opening large enough to accommodate the buret tip snugly with a very small side opening to allow escape of replaced air during titration.
Magnetic stirring bar, Teflon-sealed, Schaar.
Magnetic stirrer, variable speed.

PROCEDURE

Weigh accurately a sample of 0.3 to 0.6 gram in a 50-ml. Erlenmeyer flask. Dissolve epoxy resins in chlorobenzene, other compounds in chlorobenzene or benzene. Add 5 drops of 0.1% crystal violet indicator solution, place the rubber stopper in position, and lower the buret tip to a point just above the solution. Titrate the sample to the blue-green end point while stirring at a slow speed with the magnetic stirrer.

RESULTS AND DISCUSSION

A variety of purified epoxy compounds and commercial epoxy plasticizers were analyzed. In order to evaluate the method, especially where the purity of the epoxy sample was not known, the results were compared with those obtained by the hydrochloric acid–ethyl ether method (*11*) or the pyridinium chloride–pyridine method (*2*). The oxirane oxygen content obtained by the acetic acid–hydrobromic acid method is in excellent agreement with those obtained by the other two methods (Table I). The reaction with all compounds tested so far is almost instantaneous and proceeds at a speed equal to that of aqueous acid–base titrations. Epoxides, such as styrene oxide, which isomerize readily in acid media cannot be titrated quantitatively by this method. This is also true of other methods employing acidic reagents (*5*).

Although glacial acetic acid can be used as a solvent, in the presence of chlorobenzene or benzene sharper end points are obtained without sacrificing the speed of the reaction. Because of its greater polarity, chlorobenzene is preferable, especially in the titration of epoxy resins. In cases where desired, the titration can be followed potentiometrically using the glass-calomel electrode system as in the acetic acid–hydrochloric acid method (*4*). The sample is dissolved in 10 ml. of glacial acetic acid and a mechanical stirrer is used. Three potentiometric titration curves for a plasticizer, epoxy resins, and an epoxy compound are given in Figure 1.

The specificity of the reagent to the α-epoxy group was checked by investigating the possible interference of other functional groups. With peroxides such as oleyl peroxide, lauroyl peroxide, and benzoyl peroxide, the end points were stable for more than 5 minutes. A slow reaction of hydroperoxides was noticed but with no observable interference, as indicated by the study of mixtures of varying concentrations of cumene hydroperoxide and 9,10-epoxystearic acid and similar mixtures of *tert*-butyl peroxide and 9,10-epoxystearic acid (Table II). The end point is sharp and stable for about half a minute. The apparent reaction rate of hydroperoxides is slower than that of the oxirane oxygen and no apparent reaction of the hydroperoxide prior to the complete reaction of the epoxy group was observed.

Table I. Determination of Oxirane Oxygen by Hydrogen Bromide in Acetic Acid

Compound	% Oxirane Oxygen		
	Acetic acid–HBr[a]	Other	Theory
1,2-Epoxydodecane	8.65 ± 0.01 (6)	8.63[b]	8.68
9,10-Epoxystearic acid	5.34 ± 0.01 (6)	5.34[b]	5.32
Butyl epoxystearate	4.48 ± 0.01 (3)	4.49[b]	4.49
9,10-Epoxyocta-1-decanol	5.61 ± 0.00 (4)	5.62[b]	5.59
Cyclohexene oxide	16.22 ± 0.01 (4)	16.2[b]	16.30
Limonene monoepoxide	10.49 ± 0.02 (12)	10.44[b]	10.51
Glycidyl phenyl ether	10.58 ± 0.02 (5)	10.54[c]	10.65
Epoxy soybean oil	6.62 ± 0.00 (6)	6.5[c]	...
Epon 828	8.54 ± 0.02 (5)	8.5[c]	...
Armstrong epoxy resin C-4	9.43 ± 0.01 (6)	9.4[c]	...

[a] Figures in parenthesis represent number of determinations.
[b] Ether–hydrochloric acid method (*11*).
[c] Pyridinium chloride–pyridine method (*2*).

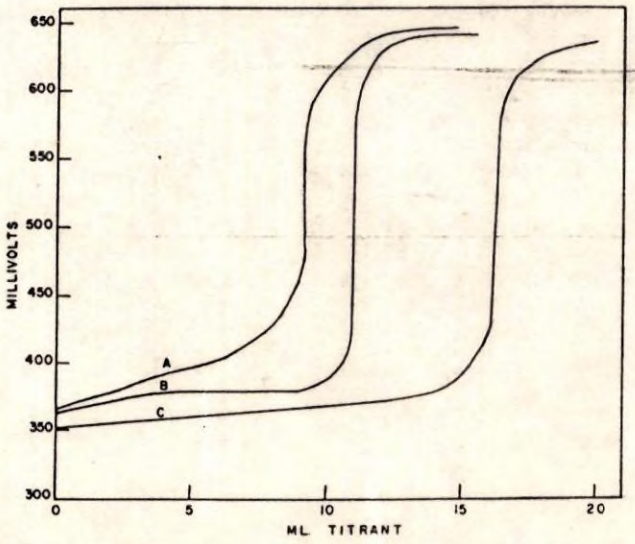


Figure 1. Potentiometric titration of oxirane oxygen by hydrogen bromide in acetic acid
A. Epon 828
B. Limonene monoepoxide
C. Epoxy soybean oil

Table II. Effect of Hydroperoxides on Oxirane Oxygen Determination by Hydrogen Bromide in Acetic Acid

Composition of Mixture, %		% Oxirane Oxygen	
9,10-Epoxystearic acid	Hydroperoxide	Calculated	Determined
99.2	0.8[a]	5.31	5.24
82.6	17.4[a]	4.43	4.37
71.9	28.1[a]	3.85	3.85
69.9	30.1[a]	5.01	4.93
49.0	51.0[a]	2.62	2.63
16.7	83.3[a]	0.89	0.95
92.9	7.1[b]	4.98	4.93
78.5	21.5[b]	4.20	4.19
53.2	46.8[b]	2.85	2.92
4.1	95.9[b]	0.22	0.28

[a] *tert*-Butyl hydroperoxide.
[b] Cumene hydroperoxide.

Other oxygenated compounds, carboxylic acids, aldehydes, alcohols, ethers, and esters were tested for interference by using 9,10-dihydroxystearic acid, 1-ketostearic acid, oleic acid, oleyl alcohol, furfuryl alcohol, dioxane, 2-butyraldehyde, benzaldehyde, eleostearic acid, butyl oleate, and methyl oleate in concentrations varying from 1 to 100%. No interference by these compounds was encountered. Solvents such as chloroform, carbon tetrachloride, and hexane did not interfere nor indicate any slowing in the apparent reaction rate of the oxirane oxygen with the titrant when present in the sample. Amines are readily titrated in glacial acetic acid and accordingly, as in the case with other oxirane oxygen methods, they interfere (*10*). The potentiometric differentiation of the amines in the presence of oxirane oxygen is possible. Although 1 to 1.5% of water does not seem to interfere, its effect on the epoxy titrations was not fully investigated and therefore it should be kept as low as possible. Acetic anhydride in general cannot be used to eliminate water. Addition of acetic anhydride resulted in poor end points and inconsistent results. Olefins were tested for possible addition of hydrobromic acid to the double bonds, with no apparent interference, and the end points were stable.

Although daily standardization of the reagent is preferable, no significant change of the titer was observed at temperatures of 25° to 27° C. and with the Karl Fischer-type buret. The method is very fast and eliminates long periods of reaction required by the indirect methods. The apparatus and technique used are simple and give excellent reproducibility when applied under the conditions described.

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