Direct Titration of Epoxy Compounds and Aziridines

SIR: The determination of the oxirane ring in organic compounds has generally involved reaction with excess hydrochloric acid in a variety of solvents. Because the reaction is slow, at least a 15-minute reaction time is generally allowed before back titrating the excess acid. The determination of aziridines also requires back-titration techniques (*1*, *4*). Durbetaki (*2*) described a direct titration of epoxies with anhydrous hydrogen bromide in acetic acid. While this method is rapid and capable of good results, the reagent, which fumes profusely in air, requires special handling and frequent restandardizations for accurate analyses.

The following method employs a stable, readily available, titrant which can be used for the direct titration of oxiranes and certain aziridines. The sample is dissolved in chloroform and titrated to a crystal violet end point with standard perchloric acid (in acetic acid or dioxane) in the presence of an excess of a soluble quaternary ammonium bromide or iodide.

For epoxides either reagent can be used, but the quaternary bromide is satisfactory for virtually all the materials usually encountered and is recommended over the iodide because of economy and better storability. With aziridines, however, the iodide is preferred as it gives more rapid reactions and sharper end points.

EXPERIMENTAL

Reagents. Standard 0.1*N* $HClO_4$ in glacial acetic acid. Mix 8.5 ml. of 72% $HClO_4$ with 300 ml. of glacial acetic acid and add 20 ml. of acetic anhydride. Dilute to 1 liter with glacial acetic acid and allow to stand overnight. Standardize against potassium acid phthalate (*3*).

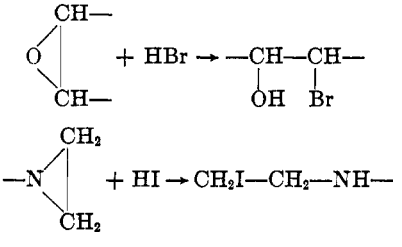
Tetraethylammonium bromide reagent. Dissolve 100 grams of NEt_4Br in 400 ml. of glacial acetic acid. Add a few drops of crystal violet indicator. Compensate for any slight indicator blank by titrating dropwise with the standard $HClO_4$ to the end point color change.

Tetrabutylammonium iodide reagent, 10% in chloroform. Dissolve 50 grams of NBu_4I (Eastman white label grade, or equivalent) in 500 cc. of reagent grade chloroform. This reagent is stable providing it is not preneutralized with perchloric acid reagent, or exposed to light. Store in the dark.

Procedure. Into a 50-ml. Erlenmeyer flask weigh a sample estimated to contain 0.6 to 0.9 meq. of oxirane or aziridine. Dissolve in about 10 ml. of chloroform. Acetone, benzene, and chlorobenzene may also be used as solubility considerations warrant. Add 10 ml. of the quaternary bromide or iodide reagent and 2 or 3 drops of crystal violet indicator. Titrate to a definite color change with standard 0.1*N* perchloric acid using a 10-ml. micro buret. Very sharp visual end points are generally obtained, especially for epoxides, but in some cases a potentiometric correlation using glass *vs.* calomel electrodes, may be desirable. The reagent blank is usually negligible, but should be checked occasionally.

DISCUSSION AND RESULTS

In the above titrations, hydrogen bromide (or iodide) generated *in situ* by the addition of perchloric acid to the quaternary ammonium halide rapidly opens the oxirane or aziridine ring



The large excess of bromide and the higher acid strength of perchloric acid afford somewhat more rapid oxirane titrations and sharper end points than those obtained with the HBr acetic acid titrant. A wide variety of epoxy compounds have been titrated by the tetraethylammonium bromide procedure with good results. Some typical data are presented in Table I. In particular, it should be noted that epoxy resins Epon 1031 and ERRA 0153 were readily analyzed by the quaternary bromide technique whereas the HBr–acetic acid method failed to give discernible end points with these solid essentially tetrafunctional resins.

Work with both oxiranes and aziridines demonstrated that HI is a more energetic ring opening agent than HBr and accordingly the quaternary iodide gives sharper end points in the perchloric acid titrations. With oxiranes this is of relatively little practical importance as the quaternary bromide system is adequate. However, for the aziridines, the more vigorous quaternary iodide–perchloric acid system is recommended. Likewise, for especially unreactive epoxides the iodide method is preferred, and in extraordinary cases an excess of perchloric acid may be added and back titrated with sodium acetate in acetic acid.

The use of acetic acid as a solvent for aziridines sometimes gives low results because of a competing proton catalyzed reaction. Only a limited number of aziridines have been investigated, but by using a solution of tetrabutylam-

Table I. Determination of Epoxy Compounds

	Epoxy Equivalent Weight			
	$HClO_4$–NEt_4Br	$HClO_4$–NBu_4I	HBr–AcOH[a]	HCl–Dioxane[b]
Epon 820 (Shell)[c]	190	...	194	193
Epon 828 (Shell)[c]	188, 186, 186, 186	186, 187, 186	...	...
Araldite TSWR-375[c] (Ciba Co.)	180, 181, 182, 180, 179	179, 179, 179, 180	...	181, 181, 181,181
Epoxy 201[d] (Union Carbide Chem. Co.)	152, 151, 151, 151	...	...	152
ERLB-0500[e] (Bakelite Co.)	113[f]	...	...	114
KP-90, Butyl epoxy stearate (Food Machinery Corp.)	418, 416, 417, 415, 418, 418, 417, 419, 418, 419	...	414, 415, 414, 413, 413, 415	420
Butyl glycidyl ether	133.5, 133.6, 133.7, 133.6	134.8, 134.0, 133.7, 134.4	...	...
Epon 1031 (Shell)[g]	257.2, 257.3, 257.4	...	Failed[h]	...
ERRA 0153[g] (Bakelite Co.)	260.0, 259.3	...	Failed[h]	...

[a] Direct titration with HBr in AcOH (*2*).
[b] Excess HCl–dioxane, back titration.
[c] Commercial epoxy resins, epichlorohydrin-bisphenol-A type.
[d] 3,4-Epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate.
[e] *p*-(2,3-Epoxypropoxy)-*N*,*N*-di-(2,3-epoxypropyl)aniline.
[f] Corrected for tertiary amine obtained by separate titration.
[g] A solid epoxy resin containing structures of the type 1,1,2,2-tetrakis(2,3-epoxypropoxyphenyl)ethane.
[h] Satisfactory analysis impossible because of poor or fading end points.

Table II. Assay of Aziridines

	Assay, wt %	
	NBu_4I–$HClO_4$	KSCN[a]
Tris-[1-(2-methyl)-aziridinyl]phosphine oxide[b]	97.4	97.2
	97.8	98.1
	98.1	97.1
		98.0
Phenyl bis[1-(2-methyl)aziridinyl] phosphine oxide[c]	97.9	99.0
	98.0	99.4
		99.4

[a] Excess aqueous HCl added in presence of excess KSCN and back titrated. A recent publication (*4*) describes a similar determination in methanol solution.
[b] MAPO, Interchemical Corp.
[c] Phenyl MAPO, Interchemical Corp.

monium iodide in chloroform the acetic acid introduced by the perchloric acid reagent did not interfere with the assays of tris-[1-(2-methyl)-aziridinyl]-phosphine oxide or phenyl bis[1-(2-methyl)aziridinyl]phosphine oxide. Some typical data are given in Table II.

For other compounds, this possible interference may dictate the substitution of a perchloric acid in dioxane reagent. Even with HI, the reaction with some aziridines may be too slow to permit direct titration; in this case, excess perchloric acid may be added and back titrated potentiometrically.

The fact that these methods are based upon nonaqueous acid–base titrimetry points out the nature of the interferences to be expected. Acids comparable to or weaker than acetic do not interfere. Bases will interfere unless correction is made. In many cases, potentiometric differentiation will be possible. For aziridines, the nature of the nitrogen in the ring-opened derivative must be considered. In the case of the phosphine oxide aziridines reported here, the resultant phosphonamide is too weakly basic to be titrated, and no interference is encountered. This will be true also for titrations of aziridinyl groups attached to carbonyl carbons. For other types in which the aziridine nitrogen is not influenced by a strong electrophilic function, its basic nature should be recognized.

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Feed Volume Corrections in Gas Chromatography

SIR: It is well known that excessive feed volume, V_f, may greatly affect the performance of elution chromatographic systems. In experimental studies of the factors affecting column efficiency, therefore, V_f must be made so small as to have no effect on the results or some correction procedure must be applied to the data to allow for the contribution of V_f to the plate height, H. So far as is known to us, tests specifically designed to ensure that the former condition applied have been conducted on only few occasions (*1*, *7*).

Recently, the second approach has become common in order to overcome experimental difficulties. This note points out that an adequate correction procedure has been theoretically established only for one form of injection, that is, where the feed band is Gaussian, and that the use of this correction procedure in general may be completely misleading. The correction procedure for a Gaussian input follows from established theory, as shown by Giddings and Robison (*4*). These authors, in practice, employed a short pre-column to convert the initial feed into a Gaussian form before injection into the study column. Then for a composite column length, L, and a pre-column length, L_1, for which the standard deviations (σ) of the emergent bands in units of time are τ and τ_1 at retention times of t and t_1, the plate height of the study column is

$$H_s = (L - L_1)\left[\frac{\tau^2 - \tau_1^2}{(t - t_1)^2}\right] \qquad (1a)$$

Provided that the pre-column produces a reasonable approximation to a Gaussian peak, Equation 1*a* is valid. Later workers (*3*, *6*) have dispensed with the pre-column and measured directly the feed volume characterized by τ_f, as the feed band passed from injection system to the column head. They then employed the equation

$$H_s = L\left[\frac{\tau^2 - \tau_f^2}{t^2}\right] \qquad (1b)$$

It is clear that while, with a pre-column, the conditions necessary to validate the use of Equation 1*a* may be approached in practice, it is by no means certain that Equation 1*b* will ever be applicable because of the difficulty of producing a Gaussian band in a simple injection system.

Consideration of available experimental information and the sequence of events in conventional injection systems, in fact, suggests that, normally, the injection profile approximates more closely a square wave (plug injection) profile than a Gaussian shape. Further, the applicability of the feed volume equation

$$V_f \leqslant \frac{2V_R'}{\sqrt{N}} \qquad (2)$$

which may be rigorously derived (*8*) from the Glueckauf square wave injection model (*5*), is widely accepted and has several times been directly tested (*1*, *2*, *7*).

The equality expressed in Equation 2 represents the upper limit of feed volume which still allows computation of the number of theoretical plates, N, via the equation

$$N = \left(\frac{V_R'}{\sigma}\right)^2 = 8\left(\frac{V_R'}{\beta}\right)^2 = 16\left(\frac{V_R'}{W}\right)^2 \qquad (3)$$

where V_R' is the total retention volume (or time), σ is the standard deviation in appropriate units, and β and W have their usual meaning. If the inequality is satisfied, in fact, the number of plates calculated from experimental data, N', is related to the true number, N, by

$$N' = N - (N_f/2) \qquad (4)$$

where N_f is the number of plates taken up by the feed band. This equation does not represent a correction. In any case, the triviality of $(N_f/2)$ in these circumstances can readily be demonstrated. For the maximum value of V_f allowed by Equation 2, it can