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Note

Gas chromatographic methods for the analysis of the halohydrins of ethylene and propylene

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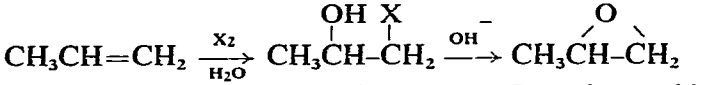
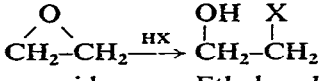
Halohydrins are important chemical intermediates in the manufacture of epoxides, especially propylene oxide[1]:



Also, halohydrins are important toxicological side products formed during sterilization with ethylene oxide and are required to be measured by the Food and Drug Administration in sterilized drugs and medical devices[2]:



It is therefore surprising that the literature is sparse in gas chromatographic (GC) methods to measure these halohydrins. Manius[2], Hartman and Bowman[3] have developed such methods but they have applied their methods only toward the measurement of a single halohydrin, the ethylene chlorohydrin (2-chloro-1-ethanol).

In this paper are reported convenient, rapid GC methods for the measurement of the halohydrins —chlorohydrin, bromohydrin and iodohydrin— of ethylene and propylene.

EXPERIMENTAL

Gas chromatography

A Varian 3700 gas chromatograph equipped with a flame-ionization detector (FID) was used. Aqueous samples (5 μl) were injected onto a glass column (1.8 m × 4 mm I.D.) packed with either Porapak R (100–120 mesh) or Tenax-GC (80–100 mesh). Column temperatures were 200°C for Porapak R and 180°C for Tenax-GC, unless otherwise noted. Carrier gas was helium at 60 ml/min, detector temperature 250°C, injector temperature 220°C. Detector attenuation 8×, range 10^{-10} A/mV.

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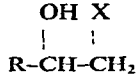
Standards

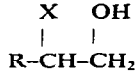
The halohydrins shown in Table I and the epoxides and glycols shown in Table II were used. All standards were prepared in aqueous solution. Concentrations were 1 mg/ml unless otherwise noted.

TABLE I

STRUCTURE AND SOURCE OF HALOHYDRINS



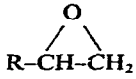
No.	*Name*	*R*	*X*	*Source*
I	2-Chloro-1-ethanol	H	Cl	Aldrich (Milwaukee, WI, U.S.A.)
II	2-Bromo-1-ethanol	H	Br	Aldrich
III	2-Iodo-1-ethanol	H	I	Aldrich
IV	1-Chloro-2-propanol	CH_3	Cl	Aldrich
V	1-Bromo-2-propanol	CH_3	Br	Aldrich
VI	1-Iodo-2-propanol	CH_3	I	Synthesized by the reaction of 1-bromo-2-propanol and iodide[4]



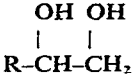
No.	*Name*	*R*	*X*	*Source*
VII	2-Bromo-1-propanol	CH_3	Br	Synthesized by the reduction of 2-bromopropionyl chloride[5]

TABLE II

STRUCTURE AND SOURCE OF EPOXIDES AND GLYCOLS



No.	*Name*	*R*	*Source*
VIII	Ethylene oxide	H	Air Products (Allentown, PA, U.S.A.)
IX	Propylene oxide	CH_3	Aldrich



No.	*Name*	*R*	*Source*
X	Ethylene glycol	H	Aldrich
XI	Propylene glycol	CH_3	Aldrich

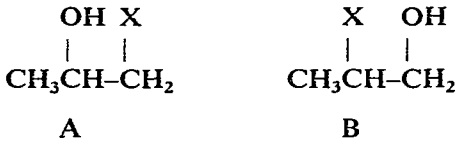
RESULTS AND DISCUSSION

Separation on porous polymer beads, such as Porapak R and Tenax-GC, occurs by the solute molecules partitioning from the gas phase into the amorphous polymer. The distinctive features of these column packings are their tolerance toward

aqueous samples and their ability to elute highly polar molecules with little or no tailing.

Either column packing can be used to resolve the halohydrins under consideration. The order of elution is chlorohydrin, bromohydrin then iodohydrin. Ethylene halohydrins elute faster than the corresponding propylene halohydrins.

Each propylene halohydrin has two positional isomers, the 1-halo-2-hydroxy isomer (A) and the 2-halo-1-hydroxy isomer (B):



A B

The two isomers for propylene chlorohydrin and propylene bromohydrin are resolved on both the Porapak R and the Tenax-GC column, with near complete resolution being obtained on the Porapak R column. Fig. 1 shows the separation of the two positional isomers for propylene bromohydrin. Isomer A elutes before isomer B. The positional isomers for propylene iodohydrin are not adequately resolved on either column. This ability to separate geometric isomers has had great utility in

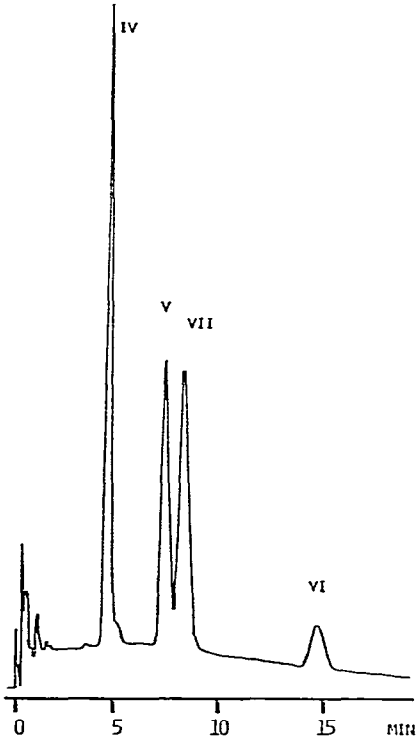
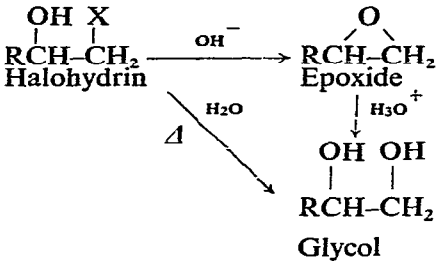


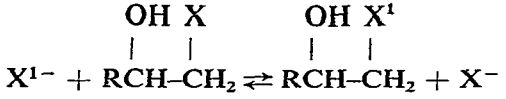
Fig. 1. Chromatogram of the propylene halohydrins using a Porapak R column. Note the resolution of the two geometric isomers of propylene bromohydrin, V and VII. Separated halohydrins: IV = 1-chloro-2-propanol; V = 1-bromo-2-propanol; VI = 1-iodo-2-propanol; VII = 2-bromo-1-propanol.

monitoring the enzymatic formation and then the resulting selective conversion to epoxide of each positional isomer[1].

Halohydrins are unstable in aqueous solution, readily converting to an epoxide or glycol:



Also, the halohydrins can undergo exchange with other halides present in the aqueous solution:



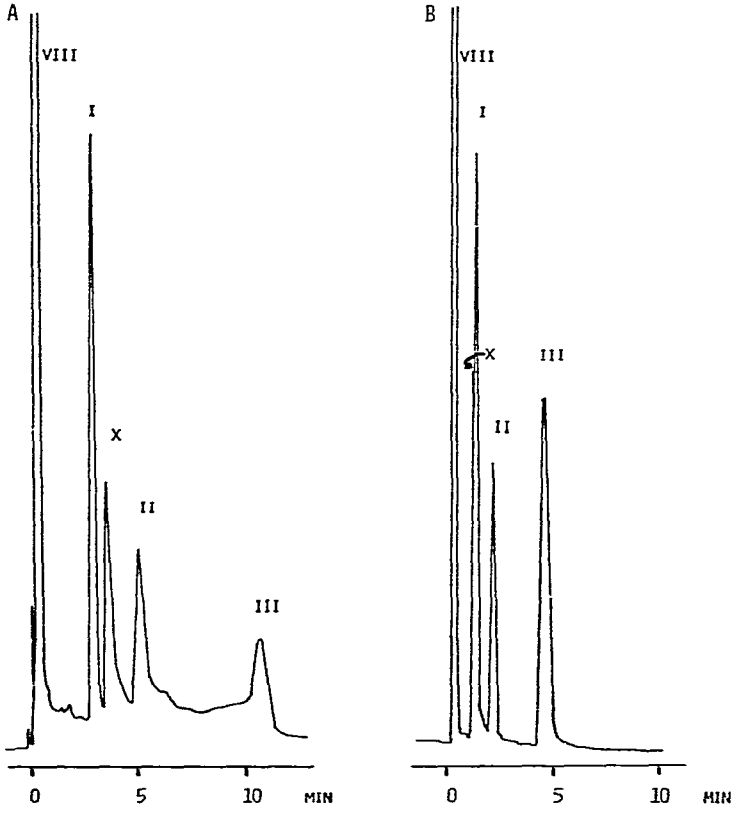


Fig. 2. Chromatograms of ethylene halohydrins and derivatives using a Porapak R column (A) and using a Tenax-GC column at 160°C (B). Separated compounds: I = 2-chloro-1-ethanol; II = 2-bromo-1-ethanol; III = 2-iodo-1-ethanol; VIII = ethylene oxide; X = ethylene glycol.

Obviously, it is important to keep track of this multitude of potential products. Figs. 2 and 3 show that either column can be used to monitor the expected products from the halohydrins.

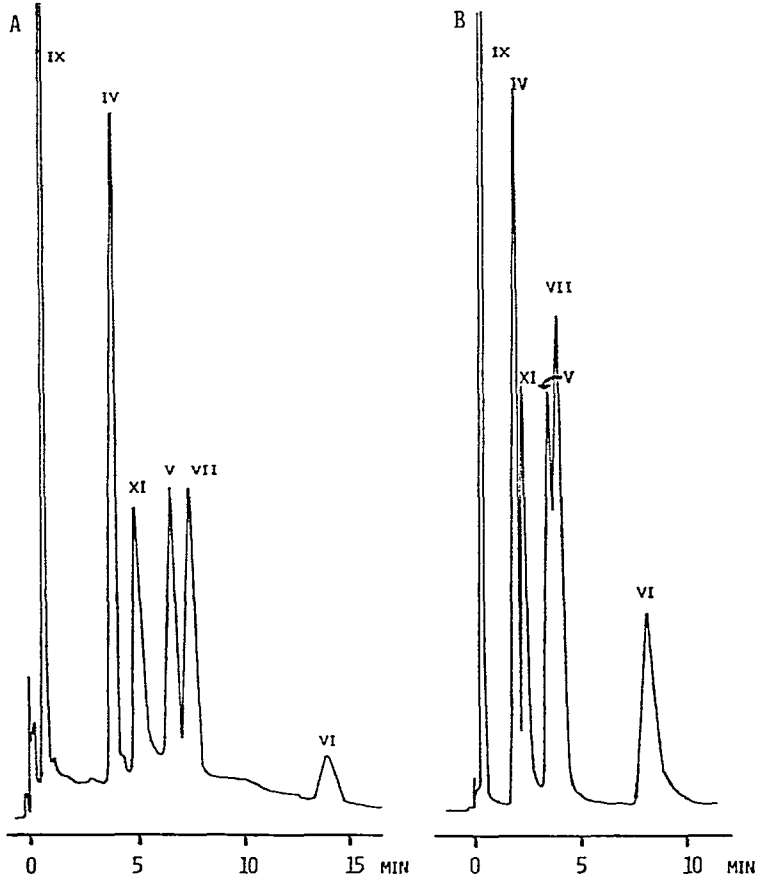


Fig. 3. Chromatograms of propylene halohydrins and derivatives using a Porapak R column (A) and using a Tenax-GC column (B). Separated compounds: IV–VII as in Fig. 1; IX = propylene oxide; XI = propylene glycol.

ACKNOWLEDGEMENT

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