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GAS CHROMATOGRAPHY–MASS SPECTROMETRY OF A SERIES OF FATTY ACID METHYL ESTER CHLOROHYDRINS AND THEIR TRIMETHYLSILYL DERIVATIVES

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SUMMARY

The reaction is reported between hydrogen chloride and a series of epoxy fatty acid methyl esters leading to the formation of mixtures of isomeric chlorohydrins. Although these chlorohydrins decomposed during gas chromatography to form oxo-compounds, their trimethylsilyl ether derivatives were found to be sufficiently stable for analysis. The mass spectra are reported for the parent chlorohydrins obtained on a direct insertion probe, and for the trimethylsilyl derivatives obtained by combined gas chromatography–mass spectrometry.

INTRODUCTION

Aliphatic epoxy compounds, and particularly expoxidised soya bean oil, are widely used as both stabilisers and plasticisers in poly(vinyl chloride) (PVC) compositions[1,2]. Although the mechanism of stabilisation is not completely understood, it is thought that reaction with hydrogen chloride (the elimination of which is the principal mode of PVC degradation) leads to the formation of chlorohydrins[3–5]. As a preliminary stage to identifying and quantifying the transformation products of epoxy compounds during PVC processing we have studied the products of reaction between a series of simple epoxy fatty acid methyl esters and hydrogen chloride in ethereal solution, and their chromatographic behaviour both underivatized and as trimethylsilyl (TMS) ethers. In addition the electron impact mass spectra have been obtained and the characteristic features which enable unequivocal identification are discussed.

EXPERIMENTAL

Preparations

Epoxides. The five epoxy fatty acid methyl esters which formed the basis of this study are listed in Table I. They were prepared from the unsaturated fatty acid methyl esters (Sigma, St. Louis, Mo., U.S.A.) by epoxidation in chloroform solution

with 3-chloroperbenzoic acid (BDH, Poole, Great Britain) using 5% molar excess of 3-chloroperbenzoic acid and allowing the reaction mixture to stand overnight at room temperature. After washing successively with equal volumes of sodium meta-bisulphite solution (5%), sodium bicarbonate (5%), and water, the solution was dried over sodium sulphate and the solvent removed by evaporation in a nitrogen stream.

TABLE I

RELATIVE RETENTION TIMES FOR EPOXIDE, OXO-, CHLOROHYDRIN AND TMS CHLOROHYDRIN FATTY ACID ESTERS

Retention times relative to methyl stearate on OV-1 column (see Experimental) isothermal at 230°.

Starting material	Relative retention time			
	Epoxide	Reaction product with HCl		TMS chlorohydrin
		Component 1 oxo-compound	Component 2 chlorohydrin	
Methyl 9,10-epoxyoctadecanoate (I)	1.55	1.65	2.57	2.79
Methyl 9,10-epoxyhexadecanoate (II)	0.91	0.94	1.44	1.58
Methyl 6,7-epoxyoctadecanoate (III)	1.54	1.58	2.47	2.72
Methyl 11,12-epoxyoctadecanoate (IV)	1.56	1.63	2.54	2.83
Methyl 11,12-epoxyeicosanoate (V)	2.69	2.80	4.75	4.94

Chlorohydrins. Small quantities of the epoxy compound (*ca.* 5 mg) in a tapered vial were dissolved in a hydrogen chloride saturated ether solution (*ca.* 0.5 ml) at room temperature, the solvent and excess hydrogen chloride being removed after a few minutes standing by evaporation in a nitrogen stream.

Trimethylsilyl ether derivatives. To small quantities of the chlorohydrins dissolved in diethyl ether (500 μl), pyridine (100 μl) and bis(trimethylsilyl)trifluoro-acetamide (10 μl) (Regis Chemical Co., Morton Grove, Ill., U.S.A.) were added, and the reaction allowed to proceed at room temperature for 30 min prior to gas chromatographic analysis.

Gas chromatography

A Pye Series 104 flame ionisation chromatograph was used throughout under the following conditions: glass column (1.5 m × 0.6 cm O.D.) packed with 3% OV-1 on Diatomite CLQ (100–120 mesh); carrier gas (oxygen-free nitrogen) flow-rate, 60 ml/min; column temperature, isothermal at 230°; detector oven temperature, 250°; injector temperature, 250°.

Mass spectrometry

Most of the mass spectra were obtained on a DuPont Model 21-490B mass spectrometer interfaced via an all-glass jet separator to a Pye 104 chromatograph. Operating conditions were the same as those above except that helium was the carrier

gas. The separator and connecting lines were held at 270 and 250° respectively and the ion source at 200°. Mass spectra were obtained at 70 eV scanning over a mass range from m/e 20–800 at 2 sec per decade. Data were acquired and processed on a VG 2020F data system. Chemical ionisation mass spectra were obtained on a Finnigan Model 1015 GC–MS system using methane reagent gas.

RESULTS AND DISCUSSION

GC–MS studies of TMS derivatives

The TMS derivatives of the chlorohydrins were found to give stable single components on gas chromatography (the retention data being given in Table I) and gave a number of characteristic fragments by combined GC–MS which are shown in Table II. Molecular ions were not present but $(M-15)$ ions as expected from TMS derivatives were observed at comparatively low intensities together with isotopic peaks indicating the presence of chlorine. The spectra of the TMS derivatives exhibited few small fragment ions, but in each case produced two characteristic ions of high abundance. These fragment ions A and B are due to cleavage between the adjacent carbons bearing the chlorine and –OTMS groups and show clearly that positional chlorohydrin isomers are produced by reaction of hydrogen chloride with the epoxides.
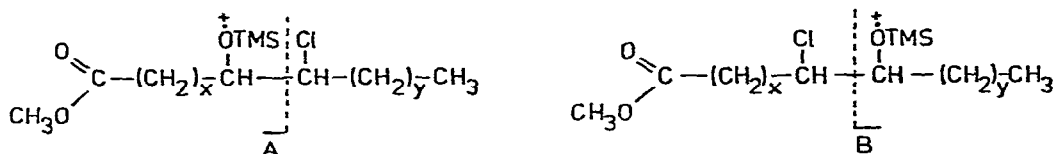

TABLE II

CHARACTERISTIC IONS FROM 70 eV FRAGMENTATION FROM TMS CHLOROHYDRINS
Spectra were obtained by combined GC–MS.

Ion	Epoxy fatty acid ester starting material									
	I		II		III		IV		V	
	m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
M — 15	405	1	377	1.8	405	2.3	405	1.1	433	1.3
A	259	100	259	99	217	100	287	85	287	100
B	215	92	187	98	257	92	187	100	215	83
A — 104	155	23	155	35	113	12	183	14	183	15

Fragment ions were also consistently produced by elimination of m/e 104 from A but their identities have not been established. A typical mass spectrum of the TMS derivative of the reaction product of HCl with methyl 9,10-epoxyoctadecanoate, contrasting with the underivatized compound, is illustrated in Fig. 1. The $M-15$ ion can be seen at m/e 405 together with its isotopic chlorine two mass units higher. Dominant peaks occur at m/e 215 and 259 by fragmentation between the carbons bearing the chlorine and oxygen (fragments A and B) enabling clear identification of the TMS chlorohydrin.
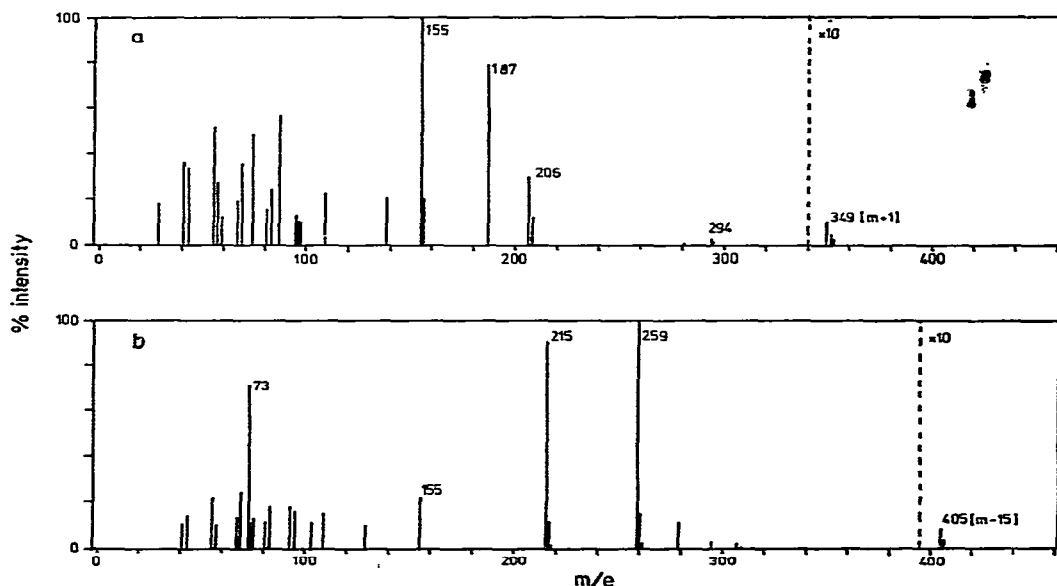
Fig. 1. Mass spectrum of the reaction product of methyl 9,10-epoxyoctadecanoate with HCl: (a) Probe introduction of chlorohydrin; (b) GC–MS of TMS derivative.

Direct insertion mass spectra

Although mass spectra of underivatized fatty acid ester chlorohydrins could not be obtained by combined GC–MS because of their decomposition, it was possible to obtain identifiable spectra by use of the direct insertion probe. The fragmentation ions which are sufficiently characteristic for identification are shown in Table III, these being typified by low intensity (M+1) ions rather than molecular ions and fragment ions C and D. C was thought to be due to $CH_3O_2C(CH_2)_xC\cdot HO^+H$ whereas although the identity of fragment D was not established it was shown to be chlorine containing (it exhibited a subsidiary ion due to isotopic ^{37}Cl at two mass units higher in all cases) and it can be seen to be derived from the acyl portion of the molecule. Fragment C showed a facile loss of 32 mass units in all cases, and a characteristic

TABLE III

CHARACTERISTIC IONS FROM 70 eV FRAGMENTATION FROM CHLOROHYDRINS
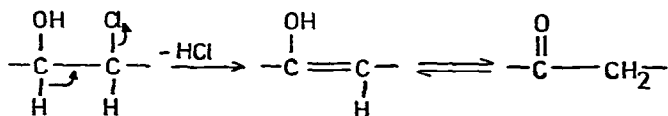Spectra were obtained by direct insertion.

Ion	Epoxy fatty acid ester starting material									
	I		II		III		IV		V	
	m/e	*%*	*m/e*	*%*	*m/e*	*%*	*m/e*	*%*	*m/e*	*%*
M + 1	349	1	321	0.3	349	0	349	0.8	377	1
C	187	80	187	50	145	100	215	50	215	69
C − 32	155	100	155	99	113	84	183	83	183	79
D	206	30	206	22	164	42	234	34	234	42
M − 54	294	3	266	1.4	294	2.7	294	2.5	322	6.4

$M-54$ ion was consistently present at low intensity although the elimination involved has not been established. The full spectrum of a typical reaction product with HCl is shown in Fig. 1, which together with the ions listed in Table III shows a number of prominent non-characteristic low fragment ions from m/e 29 to 97 which are consistently present in all the spectra.

Chromatographic behaviour of underivatized chlorohydrins

Underivatized chlorohydrins were unstable and underwent partial decomposition during injection onto the GC column. This resulted in the production of two components the first being the decomposition product, a mixture of two unresolved isomeric oxo-esters, and the second being the two unresolved parent isomeric chlorohydrins. The relative retention times of both are given in Table I. As might be expected chlorohydrin mass spectra of the second GC peak could not be obtained as further decomposition to the oxo-ester occurred during passage through the MS interface.

Evidence for the nature of the decomposition products was obtained by chemical ionisation GC–MS, by comparison of spectra of the oxo-esters with published data[6], and by trapping and re-chromatographing components. It is suggested that a possible mechanism for this facile decomposition is the elimination of HCl to form an enol which would be tautomeric with the observed oxo-ester.

$$
\begin{array}{c}
\underset{H}{\overset{OH}{\underset{|}{-C}}} \underset{H}{\overset{Cl}{\underset{|}{-C}}} - \quad \xrightarrow{-HCl} \quad \underset{H}{\overset{OH}{\underset{|}{-C}}} = C - \quad \rightleftharpoons \quad \overset{O}{\overset{\|}{-C}} - CH_2 -
\end{array}
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ACKNOWLEDGEMENT

REFERENCES

1 G. Matthews, *Vinyl and Allied Polymers*, Vol. 2, Iliffe Books, London, 1972, p. 80.
2 W. S. Penn, *PVC Technology*, Applied Science Publ., Barking, 3rd ed., 1971, p. 188.
3 A. E. Kulikova, S. B. Meiman, A. M. Shargorodskii and E. N. Zilberman, *Tr. Khim. Khim. Tekhnol.*, 3 (1972) 149.
4 J. W. Little, J. D. Farr and C. F. Huber, *Plastics Technol.*, 9 (1963) 42.
5 J. R. Startin, unpublished results.
6 R. Ryhage and E. Stenhagen, *Ark. Kemi*, 15, No. 50 (1960) 545.