

## Note

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# Speciation of polyhydroxy compounds by gas chromatography–mass spectrometry with deuterium oxide chemical ionization

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Epoxides, ethers and alcohols obtained from the reaction of epichlorohydrin (1-chloro-2,3-epoxypropane) with aliphatic alcohols are of great interest in both synthetic and industrial chemistry [1]. In general, the desired product is accompanied by a complex mixture of by-products. Even though the resulting compounds could be easily separated and detected by gas chromatography–mass spectrometry (GC–MS) with electron-impact (EI) ionization, the method fails to provide sufficient information with respect to the structure of individual compounds, partly owing to excessive fragmentation. Methane chemical ionization (CI) is another well established ionization technique, but again it provides insufficient structure-related information. An ionization method that yields intense molecular ions and simple, class-specific spectra would greatly complement former techniques in the identification of aliphatic hydroxyethers. The use of deuterium oxide as CI gas for the speciation of carbonyl compounds was described by Hawthorne and Miller [2].

The aim of this study was to exploit the potential of deuterium oxide CI for the speciation of the reaction products of epichlorohydrin with 1-butanol.

## EXPERIMENTAL

### *Chemicals*

Butoxypropanols (**3**, **5**, **6**) and their analogues (**2**, **4**) (Table I) were prepared in Drug Research Institute (Modra, Czechoslovakia) and their identity was checked by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrometry (Varian VXR 200).

Deuterium oxide (Stohler Isotope Chemicals, 99.8%) and methane (Griesheim, 99.995%) were used as CI reaction gases. Other chemicals were commercial products of the highest available purity (mostly from Lachema, Czechoslovakia) and were used as received.

### *Gas chromatography–mass spectrometry*

A Hewlett-Packard (Palo Alto, CA, U.S.A.) Model 5988A mass spectrometer equipped with dual EI–CI ion source was used to obtain the spectra. Methane CI gas

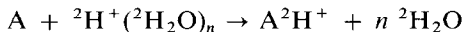
was introduced via the standard HP CI gas plumbing. Deuterium oxide was introduced directly to the ion source using the HP tuning probe (HP 5988A, opt. 32). The tuning probe needle valve was used to regulate the flow of deuterium oxide vapour to the ion source. The instrument was tuned by standard manufacturer's procedures for EI and methane CI work. In the deuterium oxide CI mode the source pressure was adjusted so as to obtain maximum abundance of the ion of  $m/z$  42  $[(^2\text{H}_2\text{O})_2^2\text{H}^+]$ . Ethyl acetoacetate, introduced via the other channel of the tuning probe, was used as a tuning compound to optimize the ion source electrode voltages. The ion source pressure in both methane and deuterium oxide CI modes was about 100 Pa.

The chromatographic separations were performed with an HP 5890A gas chromatograph equipped with an HP split-splitless multi-mode inlet operated in the splitless mode. An HP-17 column (10 m  $\times$  0.53 mm I.D.; film thickness 0.32  $\mu\text{m}$ ) (Hewlett-Packard, Vienna, Austria) was used for all separations. The column effluent was introduced into the ion source of the mass spectrometer via a *ca.* 70-cm piece of OV-1-coated 50  $\mu\text{m}$  I.D. fused-silica tubing (SGE, Australia) inserted through the standard direct capillary interface. The 50- $\mu\text{m}$  I.D. tube was coupled to the 0.5-mm I.D. megabore column by a simple T-splitter (Fig. 1). The following temperatures were used: injector, 210°C; mass spectrometer interface, 220°C; ion source, 200°C (EI) or 100°C (CI, both deuterium oxide and methane); GC oven, 2 min at 40°C then increased at 20°C/min to 220°C, held for 10 min.

## RESULTS AND DISCUSSION

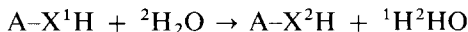
Based on published data [2-4], the following prominent processes are to be expected under deuterium oxide conditions:

(i) deuteron attachment:



(applies to all compounds ionizable by deuterium oxide CI);

(ii) hydrogen isotope exchange:



(applies to any exchangeable hydrogen, especially -OH, -NH, -SH,  $\beta$ -diketonate, etc.).

Thus, ether alcohols **3**, **5** and **6** were expected to give relatively intense

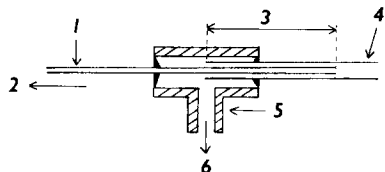
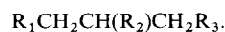


Fig. 1. Simple T-splitter. 1 = 50  $\mu\text{m}$  I.D. tube; 2 = to capillary direct interface; 3 = insertion distance about 70 mm; 4 = 0.5 mm I.D. column; 5 = Swagelock T-union; 6 = vent.

TABLE I  
COMPOUNDS USED IN THE STUDY



Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Mol.wt.
1	HO	HO	HO	92
2	C <sub>4</sub> H <sub>9</sub> O	-O-		130
3	HO	HO	C <sub>4</sub> H <sub>9</sub> O	148
4	C <sub>4</sub> H <sub>9</sub> O	HO	Cl	166
5	C <sub>4</sub> H <sub>9</sub> O	HO	C <sub>4</sub> H <sub>9</sub> O	204
6	C <sub>4</sub> H <sub>9</sub> O	C <sub>4</sub> H <sub>9</sub> O	C <sub>4</sub> H <sub>9</sub> O	260

$M + 2 + n_H$  pseudo-molecular ions ( $n_H$  being the number of exchangeable hydrogens). The spectra of compounds 1–6 under different conditions are given in Table II. Whereas the only ion of some diagnostic use in the EI spectra (70 eV) is that of  $m/z$  57, indicating the presence of (possibly) an *n*-butyl group, the molecular peak is readily distinguished in both CI modes, the difference between the methane and deuterium oxide spectra pseudo-molecular ions minus 1 giving the number of exchangeable hydrogens. For most compounds, an enhancement of the pseudo-molecular ion abundance in the deuterium oxide CI spectra is observed in comparison with the methane CI spectra. This is due to lower energy of deuterium transfer from  ${}^2H^+$  ( ${}^2H_2O$ )<sub>*n*</sub> cluster in comparison with proton transfer in the methane mode. The other ions of diagnostic use in the  ${}^2H_2O$  CI spectra are  $M + 2 + n_H - 55$  (elimination of butene) and  $M + 3 + n_H - 74$  (elimination of butanol). The power of this ionization technique together with the inertness of the GC system may be demonstrated by the fact that, under the conditions given, the GC peak of glycerol (1) gives a mass spectrum with a clearly recognizable  $M + 5$  peak [ $C_3^1H_5(O^2H)_3^2H^+$ ].

The results demonstrate the utility of deuterium oxide CI in hydroxy compound speciation.

TABLE II  
DIAGNOSTIC IONS IN THE MASS SPECTRA OF BUTOXYPROPANOL DERIVATIVES

Pseudo-molecular ions  $M + 1$  (CI gas = methane) and  $M + 2 + n_H$  (CI gas = deuterium oxide) are in italics.

Compound	<i>m/z</i> (relative intensity, %)	
	Methane CI	Deuterium oxide CI
1	<i>93(8)</i> , 75(20), 57(11), 33(100)	<i>97(7)</i> , 77(10), 75(50), 68(54), 55(100)
2	<i>131(11)</i> , 87(15), 75(100)	<i>132(35)</i> , 77(100), 76(66)
3	<i>149(19)</i> , 131(10), 93(34), 75(100)	<i>152(100)</i> , 77(61)
4	<i>167(17)</i> , 131(8), 111(59), 93(100), 75(52)	<i>169(100)</i> , 114(48), 94(38)
5	<i>205(81)</i> , 149(17), 131(53), 115(100), 75(62)	<i>207(100)</i> , 152(6), 115(37)
6	<i>261(9)</i> , 205(24), 131(39), 115(100), 75(50)	<i>262(39)</i> , 207(100), 115(78)

## ACKNOWLEDGEMENTS

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