

Fast Atom Bombardment Mass Spectrometry of Disaccharide Polyether Polyols

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Synopsis

The products resulting from the propoxylation of sucrose and lactose under alkaline conditions have been studied using FAB mass spectrometry. Soft desorption/ionization, using fast atoms, was expected to show intense protonated molecules for each component of the reaction mixture, thus allowing the extent of propoxylation to be examined under various conditions. However, it appears that addition of the FAB matrix, namely thioglycerol, prior to mass spectral analysis, resulted in alteration of the analyte via hydrolysis/dehydration, with protonated molecules appearing only for matrix/analyte reaction products, and not the original compounds which were to be examined. The resulting mass spectra, however, provided information regarding the extent of propoxylation and were consistent with results obtained by other researchers examining acetylated sugars using CI-MS.

INTRODUCTION

The rigid polyurethane foam industry uses polyether polyols from polyhydroxy compounds such as sucrose, methyl glucoside, and sorbitol to provide a rigid backbone during the polyurethane formation. The high functionality and low cost of sugars makes them ideal candidates for this purpose.

The first author has been working on the utilization of lactose, a high volume dairy waste product, for the past several years (for review see Ref. 1). More than 50 billion pounds of whey is generated as a by-product of the cheese industry, of which only 56% is being used as cattle feed or food additive. The remainder is dumped in rivers and lakes, posing a substantial pollution problem due to the high biological oxygen demand of lactose. Removal of proteins from whey results in whey permeate, which is essentially a 5% aqueous solution of lactose. It is estimated that an equivalent of 1.1 billion pounds of (solid) lactose/whey permeate is currently being dumped and wasted. Since the amount of excess lactose available in the United States amounts to more than a billion pounds, one has to think of its use in terms of a large volume chemical. One such product is the production of polyether polyols used in the making of polyurethanes used primarily for insulation.

It has been shown previously that propoxylated lactose can be used as a substitute for sucrose polyol, without any loss of physical properties in the final foam.² These polyether polyols of lactose, however, have shown unusually low

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viscosity compared to their sucrose counterparts. These polyols were not purified (decolorized), and one aim of the current work is to ascertain the effects of decolorization on formation of polyether polyols with the desired physical properties. The present work involves analysis of decolorized synthetic polyols from lactose and sucrose, utilizing fast atom bombardment (FAB) mass spectrometry. A sample of commercially available sucrose polyol was also examined for comparison. We report the apparent dehydration/hydrolysis of these polyols, which we attribute to a reaction with (or in the presence of) the thioglycerol FAB matrix liquid. In addition, we report little or no difference in the FAB mass spectra obtained from the synthetic and the commercial sucrose polyol. Somewhat larger differences observed between the two sucrose polyols, and the lactose polyol are also discussed.

EXPERIMENTAL

Polyether polyols of sugars were prepared by reacting 15 g of sugar (sucrose or lactose) with 70 mL propylene oxide in the presence of 0.4 g NaOH with 0.5 mL water in a Parr high pressure/high temperature reactor at 100°C for 20 h, until the pressure due to unreacted propylene oxide was not evident. The product was then decolorized in methanol/activated charcoal three to four times, and the solvent was evaporated under vacuum overnight. The final product was a clear viscous liquid, which was subjected to MS analysis.

MS analysis was done using Kratos MS-50 high resolution mass spectrometer, equipped with an M-Scan fast atom source and gun. The matrix was thioglycerol mixed 1 : 1 with the viscous samples directly on a copper FAB probe tip. Ionization was accomplished using 10 Kev Xe fast atoms. The instrument was operated at 6 keV accelerating voltage, and scans were acquired down from 5000 to 100 daltons at 10 s/decay using a Kratos DS-90 data system. The instrument resolution was set to about 3500.

RESULTS AND DISCUSSION

FAB MS was chosen for the analysis of the polyols because the method employs soft ionization and also because thermally sensitive compounds can be directly desorbed without heating.³ The polymerization of propylene oxide with initiation by the sugar hydroxyls should lead to a mixture of products, depending on the number of propylene oxide units attached to each hydroxyl unit of the sugar molecule, as well as possible products containing more than one propylene oxide unit per hydroxyl group. Also, initiation by the hydroxide moiety alone can result in production of polypropylene oxide. The purpose of mass spectrometry analysis was to determine if differences in the extent of formation of these various products in the synthesis of a polyol could be correlated with the mass spectral behavior. Further, the synthetic lactose polyol was compared with a sucrose polyol, prepared under identical conditions, and also with a commercial Dow sucrose polyol.

Figure 1 shows the FAB mass spectrum obtained using the Dow sucrose polyol (Voranol 440). Two series of peaks, presumed to be protonated molecules of oligomeric compounds, are readily observed, corresponding to

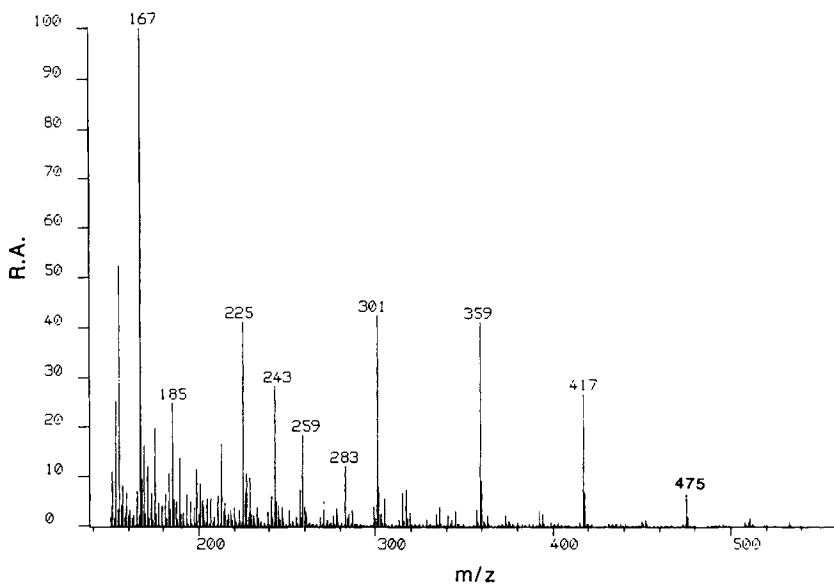


Fig. 1. FAB-mass spectrum of Dow sucrose polyol using thioglycerol as a FAB matrix liquid.

Series A: $108 + (58 \times N) + 1$ where $N = 1, 2, 3, \dots$

Series B: $108 \pm (58 \times N) + 18 + 1$ where $N = 1, 2, 3, \dots$

The series showing the largest peak at 167 daltons (Fig. 1) can be explained due to the presence of propylene oxide unit(s) attached to an extensively dehydrated monosaccharide unit (series A). A possible mechanism for the formation of this peak and other ions in this series is shown in Figure 2. Series B is attributed to serial propylene oxide addition to a dehydrated monosaccharide, with one more water than series A. The difference in the two series may be also explained by the fact that the disaccharide appears to be hydrolyzed by the thioglycerol with one of the monosaccharide units retaining the odd hydroxyl group resulting from hydrolysis of the disaccharide to monosaccharides. It also appears from the FAB mass spectra that very little polypropylene oxide (PPO) has been formed upon initiation by OH^- .

Extensive dehydration has been previously observed in the CI mass spectra⁴ of acetylated sugars. Similar results have been reported for other sugar derivatives.⁵ However, what is not clear is the origin of products resulting from the multidehydration/hydrolysis of the polyols. In the CI experiments, dehydration could result from either thermal decomposition during vaporization, or from the gas-phase ion chemistry (unimolecular fragmentation reactions) of the protonated molecule. With FAB ionization, problems associated with thermal decomposition should be significantly reduced. Sequential, rapid, unimolecular decompositions of the protonated molecule are possible using FAB ionization, although the absence of any protonated molecule is somewhat unusual. However, the loss of three (or more) neutral fragments (not radical species) via migration of a proton or larger group to give daughter ions corresponding to an extensively

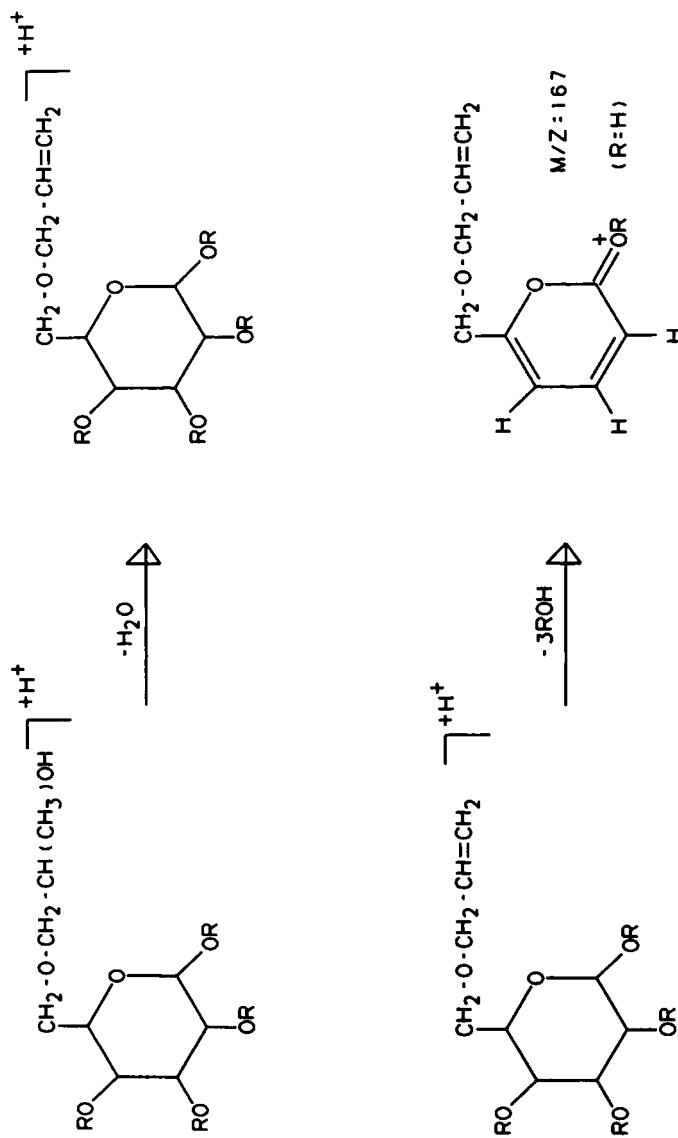


Fig. 2. Proposed method for formation of base peak $m/e = 167$. (R = H or C_3H_5)

dehydrated modified sugar, but no protonated molecule, and no fragments corresponding to loss of only one or two small neutrals, seems unreasonable based on the entropy requirements associated with unimolecular fragmentation reactions involving a rearrangement and the lifetime of ions in the source of a magnetic mass spectrometer. Alternatively, a solution-phase reaction of the polyol or the protonated polyol in the FAB matrix liquid prior to ionization could result in the observed products, and the subsequent desorption ionization process may indeed produce ions representative of those compounds actually present in FAB matrix/analyte solution as it is introduced into the mass spectrometer. Such an explanation is not unprecedented. For example, we have shown that the thioglycerol reacts with some *N*-oxides via a solution-phase reduction to give an apparent loss of 16 daltons from the expected FAB produced protonated molecule, which is actually a protonated molecule for the reduced compound rather than a fragment ion.⁶ Attempts to sort out this problem using a weaker acid (glycerol) as the FAB matrix liquid have been unsuccessful, because, although the same ion series are seen using glycerol, the overall signal level is extremely low (spectra not shown). Furthermore, the rate of reaction appears so rapid that temporal changes in the mass spectra can not be used to monitor the proposed solution-phase hydrolysis/dehydration reactions attributed to the FAB matrix. It should also be mentioned that the lack of any protonated molecule from sucrose polyol, by CI-MS, was also reported by Japanese researchers, but no details of fragment ion intensities were given.⁷

Figures 3 and 4 show the FAB mass spectra obtained for synthetic sucrose polyol and lactose polyol, respectively. For the sucrose polyol, two major series which correspond to the A and B series found earlier are present. In addition, a series that corresponds to $(58) \times N + 1$, probably arising from polypropylene oxide chains (m/e 175 largest peak) is found, and lastly there is a series cor-

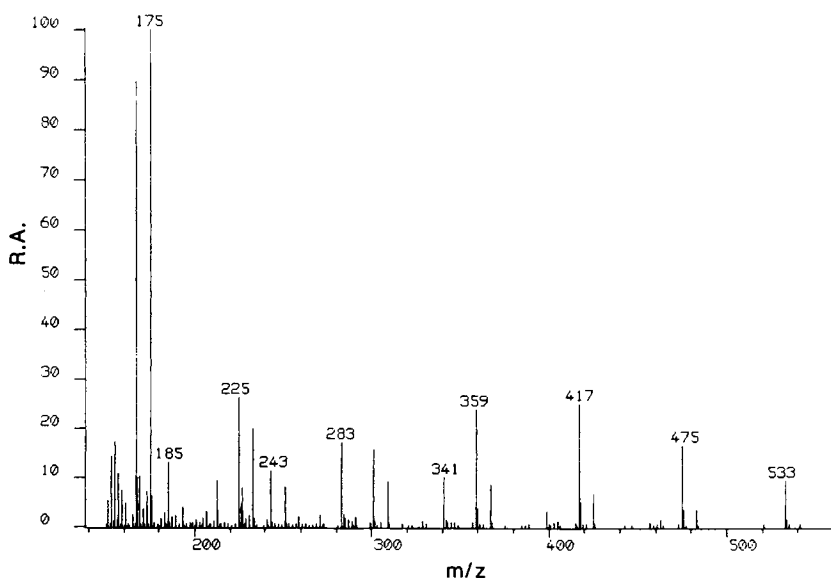


Fig. 3. FAB-mass spectrum of synthetic sucrose polyol using thioglycerol as a FAB matrix liquid.

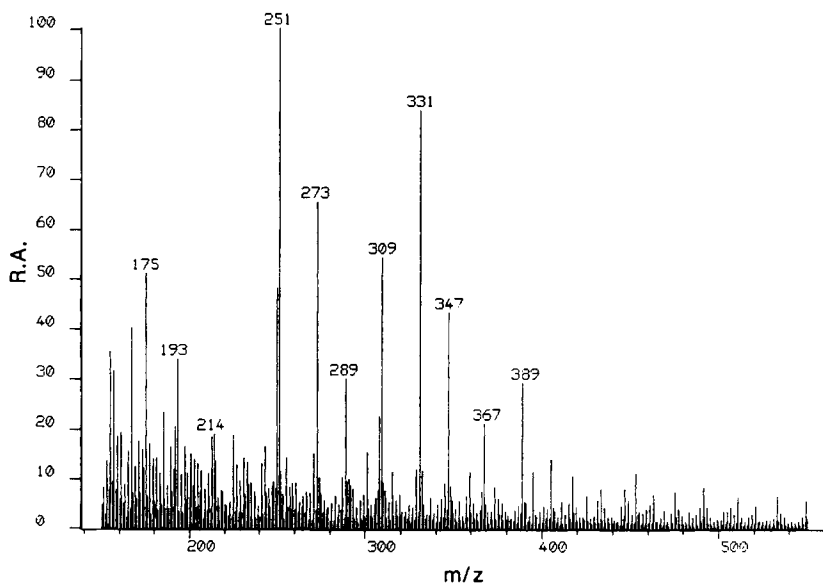


Fig. 4. FAB-mass spectrum of synthetic lactose polyol using thioglycerol as a FAB matrix liquid.

responding to $(58) \times N + 18 + 1$, which shows maximum intensity at 209 daltons.

For lactose polyol a similar fragmentation pattern is obtained. However, the ratios of the products are different. A series with the largest peak at 167 daltons is again attributed to $108 + (58 \times N) + 1$ corresponding to series A for sucrose polyether polyol. The largest peak at 251 daltons belongs to a series given by $(58 \times N) + 18 + 1$, and another series including the large peak at m/e 331 to $(58 \times N) - 18 + 1$.

Normalization of the peak intensities, based on total ion current for the protonated molecules of all the respective ion series and the relative percentages of the ion intensities in each ion series, should enable us to estimate the relative ratios of products formed by reaction initiated by sugar hydroxyls versus that initiated by OH^- . Also, the average number of polypropylene units attached per sugar molecule, and the extent of the side reaction, formation of PPO, should be reflected in the intensities observed in the FAB mass spectra. This work is currently under way.

CONCLUSION

In conclusion, it can be stated that, even though FAB is a soft ionization technique which usually shows intense protonated molecules, the ions observed in the spectra of the three polyols were not consistent with the known structures. This unexpected mass spectral behavior is attributed to extensive dehydration of the propoxylated sugar (Fig. 2) after addition to the thioglycerol FAB matrix liquid. We have already shown the absence of $\text{C}=\text{C}$ in lactose polyether polyols, by NMR and IR.⁸ Because polyols are generally complex mixtures that can be

separated only with great difficulty, soft ionization MS is inherently suitable for product characterization if protonated molecules can be observed from each component of the oligomeric series. Such ion series were observed with the three sugar polyols examined in this study. Although they resulted from dehydration after hydrolysis to monosaccharides, these ion series nevertheless can be interpreted as belonging to the few ion series that differ by a mass of 58 daltons (propylene oxide) with addition or subtraction of a mass of 18 daltons (water). The series can be used to compare the polyols obtained from various sugars. For example, the FAB mass spectra of the synthetic, decolorized sucrose polyol, and the commercial sucrose polyol were very similar, showing the same ion series, A and B, and similar abundances (Figs. 1 and 3). The synthetic lactose polyol also showed these ion series, especially the A series, but differences in the ion abundances were readily apparent (Fig. 4). The extent of formation of unwanted polypropylene oxide polymers can be readily determined, as can, in principle, the average number of propylene oxide units added (or the molecular weight) based on the apparent average value of N .

Quantitative and further analysis to show correlations between polyol product composition and mass spectral behavior are under way in our laboratories.

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