

PYROLYSIS AND MASS SPECTRA OF TRIMETHYLSILYL DERIVATIVES OF MONOSACCHARIDES

C. Shimasaki, T. Kanaki, S. Takeuchi⁺, K. Hasegawa, D. Horita, E. Tsukurimichi and T. Yoshimura

Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, Gofuku, Toyama-shi 930

⁺Faculty of Education, Toyama University, Gofuku, Toyama-shi 930, Japan

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Abstract

The pyrolysis of trimethylsilyl derivatives of saccharides (1) was investigated by DTA-TG, MS, GC/MS and TG-GC/MS. The DTA-TG/DTG curves showed that the pyrolysis of 1 occurred in one stage. The exothermic peaks were due to sublimation or thermal decomposition by vaporization. The cleavage mechanism by electron impact of 1 was classified into four categories: 1) stepwise elimination of the side-chain, 2) cleavage of the side-chain, 3) cleavage of the pyranose ring, and 4) cleavage of the pyranose ring and side-chain at the same time. The mass-spectrum for 1 revealed the main common four fragment ions, such as m/z 73, 191, 204 and 217, with cleavage of the pyranose ring. These fragment ions were detected with a similar retention time in the gas chromatogram by GC/MS or TG-GC/MS. The retention time for 1 increased in the sequence aldopentose < ketohexose < aldohexose. This result indicates that the trimethylsilyl derivatives are thermally stable. Subsequently, the pyrolysis regime for 1 obeyed apparent 1/2-order kinetics and their apparent activation energy was estimated as 75–100 kJ/mole.

Keywords: mass spectra, pyrolysis, trimethylsilyl derivatives of monosaccharides

Introduction

The trimethylsilyl derivatives of saccharides (1) have many advantages over any other substitutes. Furthermore, it appeared that 1 would be potentially useful for gas chromatography [1]. Again, the requirement of only submicrogram amounts of the material for a mass spectrum and the possibility of an analysis with a gas chromatograph directly coupled to it present obvious advantages for the study of trimethylsilyl ethers [2]. Mass-spectral data on 1 were first published [3] in 1967, when derivatives of disaccharides were examined. A mass-spectrometric study of carbohydrates as trimethylsilyl ethers, and the use of mass

spectrometry to determine trimethylsilyl derivatives of purified crystalline sugars and the fragmentation of these compounds have been reported [4].

Thermal analysis has been used mainly to examine the thermal behavior of free monosaccharides and 1. In the present study, however, the pyrolyses of these compounds were examined in order to establish their thermal stability. The application of DSC to study these pyrolysis processes provides enough information to establish kinetic relation between kinetic constant K and temperature, for instance, whereby the activation energy concerned can be calculated.

Experimental

Materials

All monosaccharides such as *D*-glucose (a), *D*-galactose (b), *D*-fructose (c), *D*-xylose (d) and *L*-arabinose (e) used in this study were of analytical grade and were used without further purification. Hexamethyldisilazane and trimethylchlorosilane were obtained from Tokyo Kasei Co. Solvents were of reagent grade and were used as supplied unless specifically noted.

Trimethylsilylation reaction

Trimethylsilyl (TMSi) derivatives of five monosaccharides (1a~1e) were prepared by methods described by Sweeley *et al.* [4] or an analogous method. The standard conditions for trimethylsilylation were adopted as a result of these studies, as follows. About 100 mg of monosaccharide was treated with 10 ml of anhydrous pyridine, 3 ml of hexamethyldisilazane and 3 ml of trimethylchlorosilane. The mixture was vigorously shaken for about 1 min and then allowed to stand at room temperature for 30 min, after which 50 ml of water and 50 ml of chloroform were added with vigorous stirring. The TMSi derivatives were extracted twice with 50 ml portions of chloroform. The combined chloroform solution was evaporated under reduced pressure to give a colorless viscous oil.

Measurements

Thermal analysis was performed by using a Rigaku Denki TG-DTA and DSC apparatus in air at a heating rate of 5 deg·min⁻¹. TG-TRAP-GC/MS and GC-MS were carried out with the Shimadzu combined system in stationary helium gas at a heating rate of 10 deg·min⁻¹. Mass spectra were taken at an ionization potential of 20 eV, using a JEOL-JMS-D300.

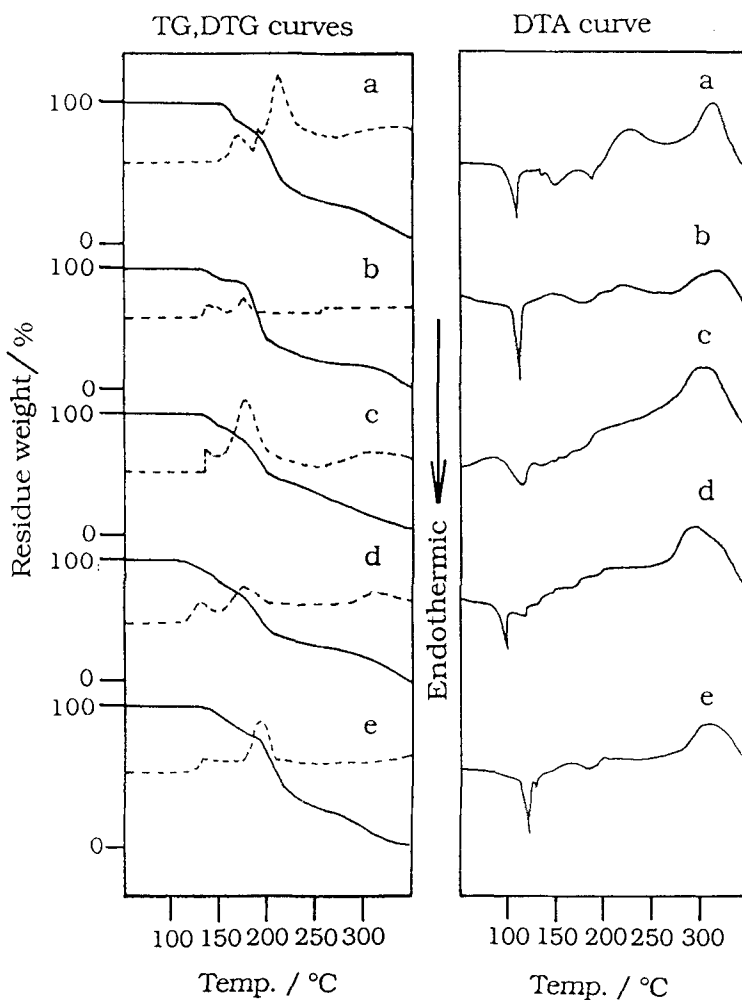


Fig. 1 TG, DTG and DTA curves for monosaccharides; a) *D*-glucose; b) *D*-galactose; c) *D*-fructose; d) *D*-xylose; e) *L*-arabinose. Heating rate: 5 deg·min⁻¹

Results and discussion

Thermal behavior

Figure 1 shows TG/DTG-DTA curves for monosaccharides. These DTA curves exhibited an exothermic peak at the melting point and exothermic peaks attributed to thermal decomposition by vaporization, with a mass loss of about 90% in the temperature region of 150 to 250°C. The TG curves show that the pyrolysis of monosaccharides takes place in several stages. On the other hand,

for 1 the DTA curves exhibited one exothermic peak, as shown in Fig. 2. The TG curves show that the pyrolysis of 1 takes place at the exothermic peak. This result was confirmed by MS, TG-GC/MS and DSC, as will be discussed later.

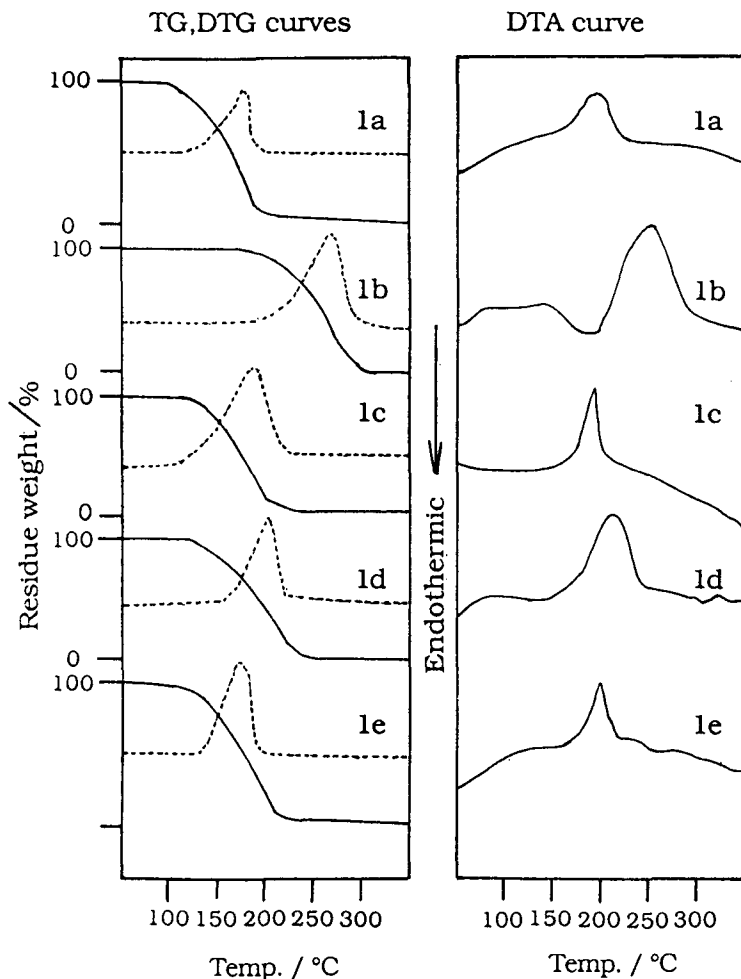


Fig. 2 TG, DTG and DTA curves for 1; 1a) *D*-glucose-TMSi; 1b) *D*-galactose-TMSi; 1c) *D*-fructose-TMSi; 1d) *D*-xylose-TMSi; 1e) *L*-arabinose-TMSi. Heating rate: 5 deg·min⁻¹

The fragmentation mechanism of TMSi derivatives

The mass spectral data were measured by electron impact with regard to the main fragment ions of 1. The structure and the cleavage mechanism of each fragment ion were investigated by high-resolution mass spectroscopy. Molecular ions are not observed in the mass spectra of 1, but an intense peak is present

because of the loss of a CH_3 radical from one of the TMSi groups; from this, the molecular weight can be determined. This 'M-15' ion fragments of 1 cleave further by stepwise elimination of two molecules of trimethylsilanol (TMSiOH), similarly as in the pathway described by Sweeley *et al.* [4]. The base peaks of 1a, 1b and 1e appeared at m/z 204 ($\text{C}_8\text{H}_{20}\text{O}_2\text{Si}_2$); it could be observed for other derivatives too. The base peak of 1c and 1d appeared at m/z 217 ($\text{C}_9\text{H}_{21}\text{O}_2\text{Si}_2$). Unique peaks at m/z 73 ($\text{C}_3\text{H}_9\text{Si}$) and m/z 191 ($\text{C}_7\text{H}_{19}\text{O}_2\text{Si}_2$) were observed for 1. The main fragment ion of 1a is shown in Figs 3 and 4. The cleavage mechanisms by electron impact of their materials were classified into the following four categories (the m/z data in the following categories are the values corresponding to the fragment ion in Figs 3 and 4):

- 1) Stepwise elimination of the side-chain from the pyranose ring: m/z 525, 435 and 345.
- 2) Cleavage of the side-chain: m/z 73.
- 3) Cleavage of the pyranose ring: m/z 333, 319, 305, 279, 217, 204 and 147.
- 4) Cleavage of the pyranose ring and the side-chain at the same time: m/z 191.

These fragment ions indicate that a TMSi group of the derivative cleaved briefly during electron bombardment and the cleavage of the pyranose ring continued. In the thermal decomposition of 1, two major peaks were separated by gas chromatography. Table 1 also shows data of a gas chromatogram relating to the thermal decomposition of 1.

Thermogravimetric analyzer-gas chromatograph-mass spectrometer system

In order to investigate the pyrolysis of 1 giving the DTA and TG curves described above over the range from 150 to 300°C, GC/MS (Method A) and TG-TRAP-GC/MS (Method B) were carried out in an atmosphere of stationary helium.

Figure 5 shows the gas chromatogram of 1 obtained by Method A. Some peaks were observed at a retention time of 18 min for an aldopentose such as 1d or 1e, of 22 min for a ketohexose such as 1c, and of 25 min for an aldohexose such as 1a or 1b. The retention times of 1a and 1b, and of 1d and 1e, differed slightly. The TMSi derivative of a monosaccharide possesses an inherent retention time and can be separated by gas chromatography. It is apparent from these results that the retention time for 1 increased in the sequence aldopentose < ketohexose < aldohexose.

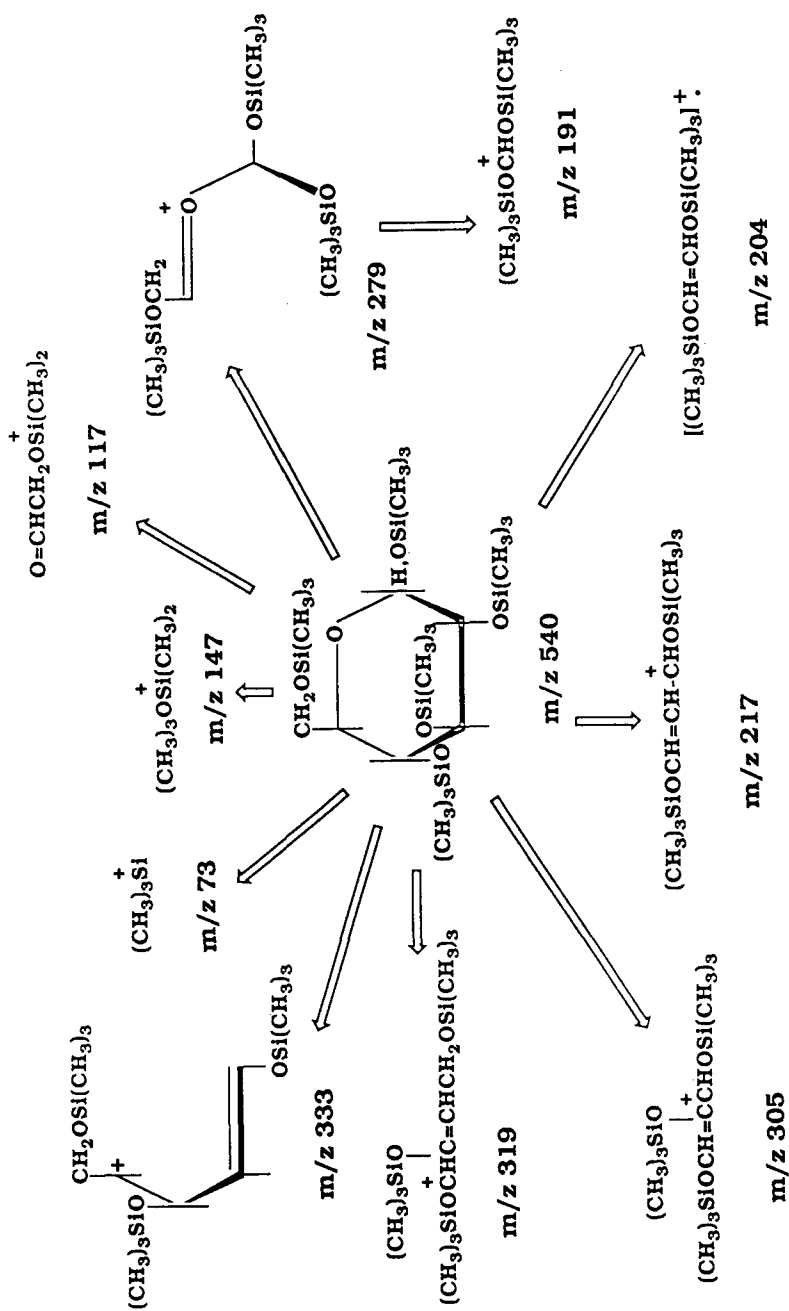


Fig. 3 Cleavage mechanism using EI method for 1a

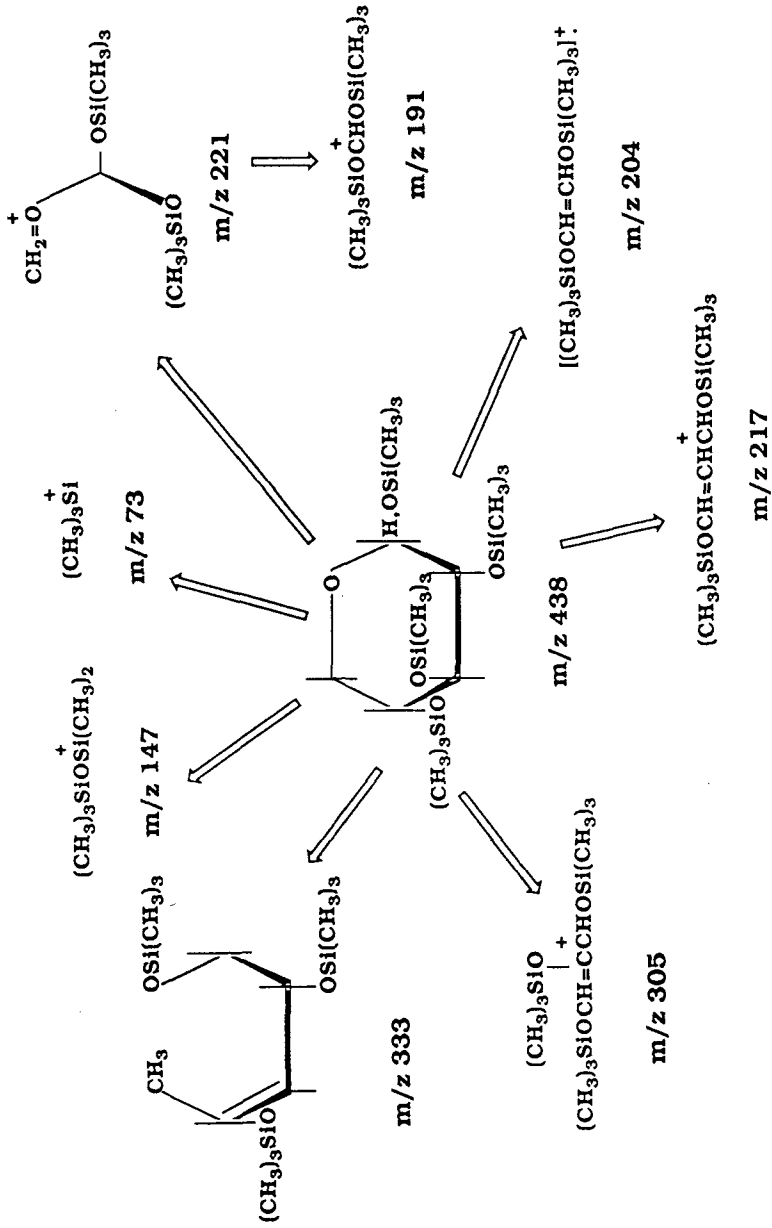


Fig. 4 Main fragmentation for 1a

Figure 6 shows mass spectra on the gas chromatogram of 1a in two peaks. The characteristic fragment ions described in Fig. 4, i.e. m/z 73, 191, 204 and 217, were observed in each case. The spectrum at m/z 473 was observed for the first peak only, indicating a complete TMSi derivative.

Table 1 Mass spectral and mass chromatogram data for 1

Compound	Mass spectral data (EI method)			GC/MS spectral data	
	m/z	Relative intensity	Probable ion composition	Retention time/min	m/z
1a	73	91.1	C ₃ H ₉ Si	23.8	73, 191, 204, 217
	117	29.2	C ₅ H ₁₃ OSi		319, 437
	191	1000.0	C ₇ H ₁₉ O ₂ Si ₂		
	204	over	C ₈ H ₂₀ O ₂ Si ₂	25.1	73, 191, 204, 217
	217	374.0	C ₉ H ₂₁ O ₂ Si ₂		319
	305	25.5	C ₁₂ H ₂₉ O ₃ Si ₃		
	319	20.8	C ₁₃ H ₃₁ O ₃ Si ₃		
	333	17.0	C ₁₄ H ₃₃ O ₃ Si ₃		
1b	73	56.6	C ₃ H ₉ Si	22.8	73, 191, 204, 217
	191	1000.0	C ₇ H ₁₉ O ₂ Si ₂		319, 437
	204	over	C ₈ H ₂₀ O ₂ Si ₂		
	217	605.8	C ₉ H ₂₁ O ₂ Si ₂	23.8	73, 191, 204, 217
	305	37.4	C ₁₂ H ₂₉ O ₃ Si ₃		319, 437
	319	36.5	C ₁₃ H ₃₁ O ₃ Si ₃		
1c	73	317.5	C ₃ H ₉ Si	21.5	73, 191, 204, 217
	191	66.9	C ₇ H ₁₉ O ₂ Si ₂		
	204	709.2	C ₈ H ₂₀ O ₂ Si ₂	22.7	73, 191, 204, 217
	217	1000.0	C ₉ H ₂₁ O ₂ Si ₂		319, 437
	305	42.5	C ₁₂ H ₂₉ O ₃ Si ₃		
	319	47.1	C ₁₃ H ₃₁ O ₃ Si ₃		
1d	73	77.4	C ₃ H ₉ Si	19.8	73, 191, 204, 217
	191	537.0	C ₇ H ₁₉ O ₂ Si ₂		
	204	1000.0	C ₈ H ₂₀ O ₂ Si ₂	20.9	73, 191, 204
	217	572.0	C ₉ H ₂₁ O ₂ Si ₂		
	333	16.6	C ₁₄ H ₃₃ O ₃ Si ₃		
1e	73	267.9	C ₃ H ₉ Si	17.7	73, 191, 204, 217
	191	451.0	C ₇ H ₁₉ O ₂ Si ₂		
	204	548.9	C ₈ H ₂₀ O ₂ Si ₂	19.4	73, 191, 204, 217
	217	1000.0	C ₉ H ₂₁ O ₂ Si ₂		
	333	28.1	C ₁₀ H ₂₂ O ₂ Si ₂		

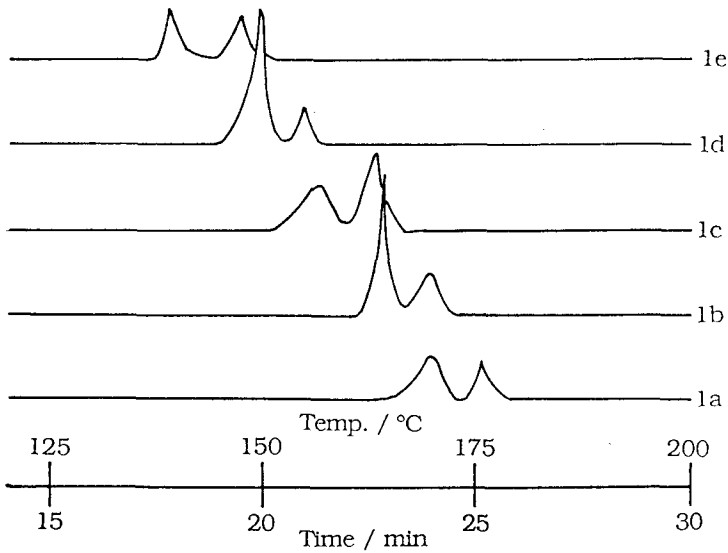


Fig. 5 Mass chromatogram of 1 with GC/MS (Method A)

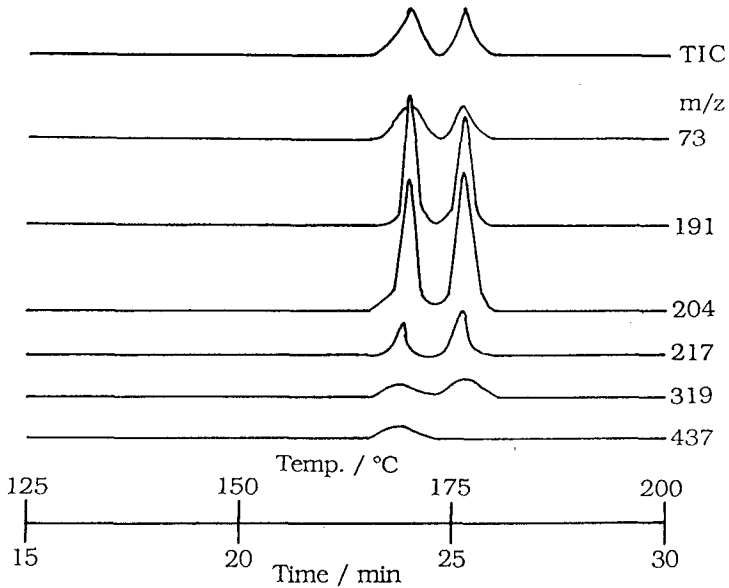


Fig. 6 Mass chromatogram of 1a with GC/MS (Method A)

In Method B, the pyrolysis products were collected and analyzed by GC. This method was applied to the analysis of thermal degradation products of 1. Figure 7 shows the gas chromatogram of 1, and Fig. 8 that of the thermal de-

composition products of 1a. In Fig. 8, the gas chromatogram of 1a contained some peaks with retention times different from those of the peaks obtained by

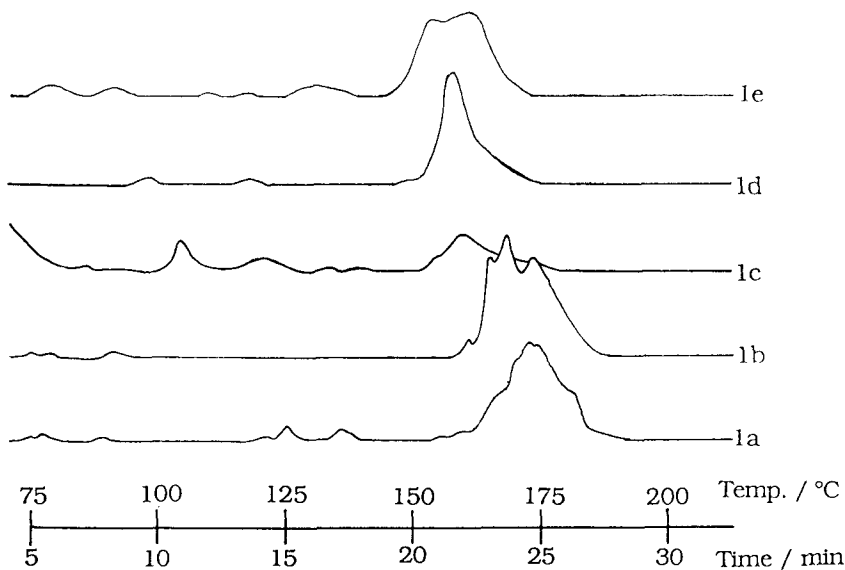


Fig. 7 Mass chromatogram of 1 with TG-TRAP-GC/MS (Method B)

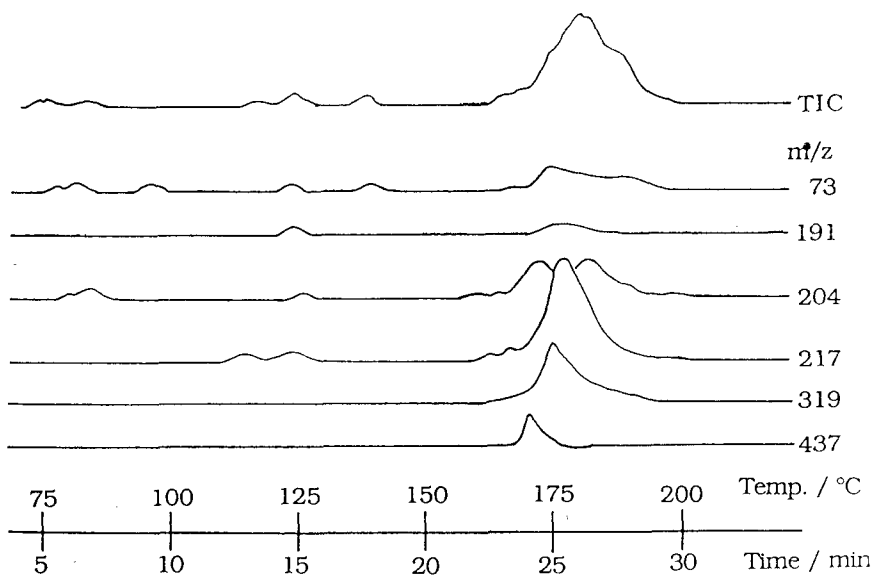


Fig. 8 Mass chromatogram of decomposition products of 1a with TG-TRAP-GC/MS (Method B)

Method B; other derivatives were similar. This indicated a low degree of trimethylsilylation in 1a. Figure 8 shows that each mass spectrum after thermal degradation is identical to the corresponding mass spectrum, e.g. m/z 204, 217, 437, etc., as shown in Fig. 6. The TMSi derivatives were thermally stable, but the separation of 1 on a gas chromatogram was difficult by Method B.

Kinetic analysis of the thermal decomposition

The kinetics of thermal decomposition of 1 was studied by direct thermal measurements, using DSC. Each sample, weighing approximately 5–15 mg,

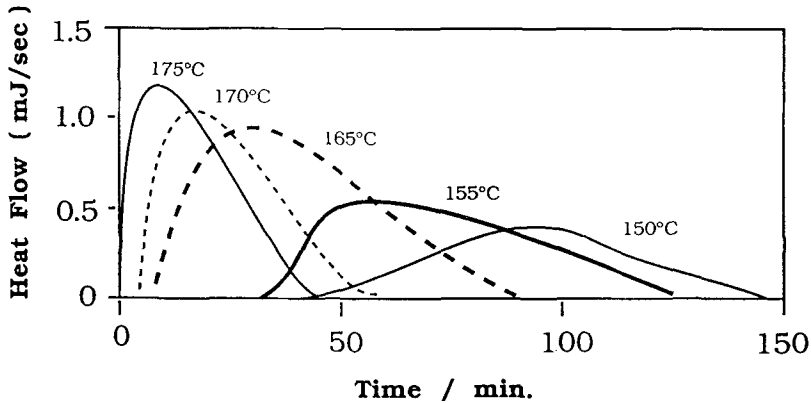


Fig. 9 Isothermal polymerization curves of 1e at 150, 155, 165, 170 and 175°C

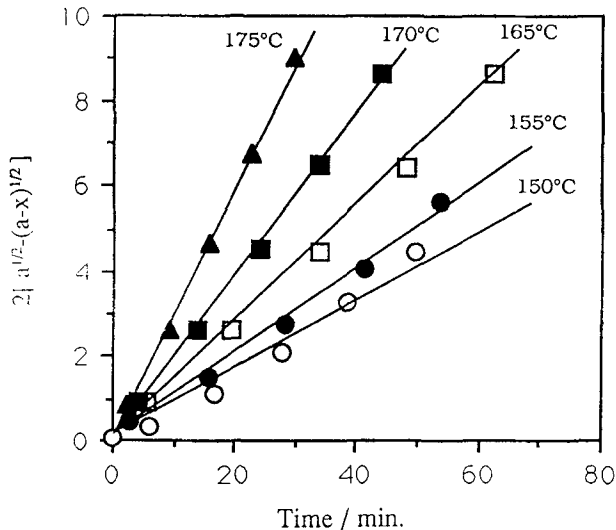


Fig. 10 $1/2$ -order kinetic plots of $2[a^{1/2} - (a-x)^{1/2}]$ vs. t , the time after t_0 , the induction period, for isothermal polymerizations

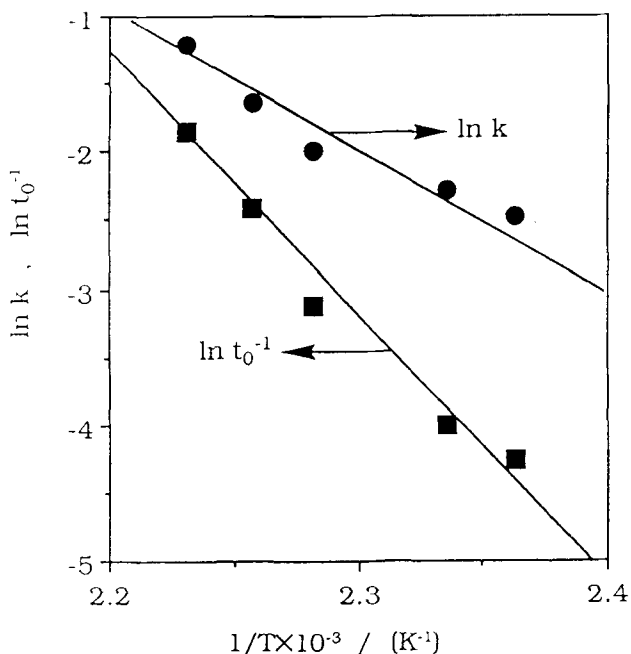


Fig. 11 Arrhenius plots of 1/2-order rate constants, k , vs. temperature and induction period t_0 vs. temperature

was sealed in an aluminum pan and DSC measurements were carried out by using the isothermal mode.

Figure 9 shows the isothermal polymerization curves for 1e at 150, 155, 165, 170 and 175°C. After an induction period, the exothermic heat of the thermal decomposition rose to its maximum, and then decreased to zero in the final stage of the process. Analysis of the isothermal curve for 1e shows that the thermal decomposition regime does not obey apparent first-order kinetics. For a given isothermal curve and x , the fractional area up to time t , a 1/2-order kinetic plot of $2(a^{1/2} - (a-x)^{1/2})$ vs. t is linear for each curve. Figure 10 shows these plots for five samples of 1e at 150, 155, 165, 170 and 175°C. Arrhenius plots of k and t^{-1} are shown in Fig. 11. These data do not agree with the induction period data of Arrhenius plots of t_0^{-1} and t^{-1} .

Table 2 Kinetic data for the pyrolysis process of 1

	$E_a / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta S / \text{J} \cdot \text{K}^{-1}$
<i>L</i> -Arabinose-TMS	75.2	-100.0
<i>D</i> -Glucose-TMS	77.6	-106.2
<i>D</i> -Galactose-TMS	102.0	-47.4

These data suggest that the plots in Fig. 10 obey 1/2-order kinetic equations, and the reactions occur as thermal decompositions accompanied by volatility. The exothermic peaks of 1a and 1b do not represent the induction period for the volatility of 1. As shown in Table 2, the activation energy of the thermal decomposition was calculated from the Arrhenius plots. The activation energy of 1b is a higher than those for 1a and 1e. This indicates thermal instability for the low-degree trimethylsilylation of 1b. The authors expect the activation energy of 1 to be approximately 75~100 kJ/mole, causing partial pyrolysis.

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References

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Zusammenfassung — Mittels DTA-TG, MS, GC/MS und TG-GC/MS wurde die Pyrolyse von Trimethylsilylderivaten von Sacchariden (1) untersucht. Die DTA-TG/DTG-Kurven zeigten, daß die Pyrolyse von (1) in einem Schritt stattfindet. Die exothermen Peaks sind der Sublimation oder der thermischen Zersetzung durch Verdampfen zuzuschreiben. Der Abspaltungsmechanismus durch Elektronenstoß von 1 kann in vier Kategorien unterteilt werden: 1) schrittweise Eliminierung der Seitenkette, 2) Abspaltung der Seitenkette, 3) Abspaltung des Pyranoseringes und 4) gleichzeitige Abspaltung von Pyranosering und Seitenkette. Das Massenspektrum von 1 zeigt die vier häufigsten Fragmentionen mit m/z 73, 191, 204 und 217 bei Abspaltung des Pyranoseringes. Diese Fragmentionen werden für 1 mit einer ähnlichen Retentionszeit detektiert, ansteigend in der Reihenfolge Aldopentose Keto-hexose Aldo-hexose. Dieses Ergebnis zeigt die thermische Stabilität der Trimethylsilylderivate. Anschließend unterliegt das Pyrolysesystem einer scheinbaren Reaktionsordnung von 1/2 und die scheinbare Aktivierungsenergie wurde mit 75~100 kJ·mol⁻¹ geschätzt.