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Thermogravimetric Analyzer(TG)-Gas Chromatography(GC)/Mass Spectrometry(MS) and Pyrolytic Studies of 1,6-Bis(2-oxooxazolidin-3-ylcarbonylamino)hexane

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1,6-Bis(2-oxooxazolidin-3-ylcarbonylamino)hexane (**1**) was prepared from 2-oxazolidinone and hexamethylenediisocyanurate using triethylenediamine as a catalyst in benzene. A TG effluent gas is collected in a cold trap and then directly injected into a GC for separation, the MS for unequivocal identification. The 13 effluent compounds from the thermal degradation of **1** were identified.

Preparation and thermal properties of Poly(2-oxazolidinone)s are the subjects of recent interest.[1] The Poly(2-oxazolidinone)s have been most extensively studied, and their preparations by various methods[2-5] have been reported. However, their thermal behaviors were not fully explored. The present authors now report a new thermal data to give the knowledge of identifying the thermal degradation products. Previously one of the authors has reported briefly the thermal behavior of Poly(2-oxazolidinone)s, prepared by the reaction between tris(2,3-epoxypropyl)isocyanurate and hydroquinone or resorcine with sodium hydroxide as a catalyst in refluxing N,N-dimethylformamide.[6] In this paper, the present authors describe the thermal behavior of **1** prepared by the reaction 2-oxazolidinone with hexamethylenediisocyanurate in the presence of triethylenediamine under refluxing 50 mL of benzene solution under nitrogen atmosphere. The identification of **1** was readily confirmed by the spectral data and elemental analysis. The results of the thermal analysis (TG-DTA) of **1** in a stream of dry nitrogen gas are shown in

Fig. 1. Three endothermic breaks, at 126.2, 236.8, and 371.4 °C, were observed. The endothermic break at 126.2 °C was apparently attributable to the melting of 1. The TG curve shows that the pyrolysis process for a sample takes place in two stages. In order to investigate the thermal decomposition processes causing the DTA breaks and the TG curve in the range from 200 to 500 °C, TG-TRAP-GC/MS[7] and TG-MS were both carried out in stationary He gas. Among these thermal instruments, the TG determines the weight loss of sample as a fuction of temperature. This is especially useful for the study thermal degradation of the sample. By itself, of course, TG does not have the capability of identifying the thermal degradation products. Coupling of a TG to a MS has been reported. The effluent gas from a TG is directly introduced into a mass spectrometer for analysis. However, in many cases the TG effluent gas is a highly complex mixture. Identification of less aboundant components is rather difficult and often overlooked. In addition, quantitative estimation of the constituents is very difficult. Another approach is to collect the pyrolysis products and then analyze this collected material by a GC. This method has been applied to the analysis of thermal degradation products of samples.[8-11] The present authors have coupled three

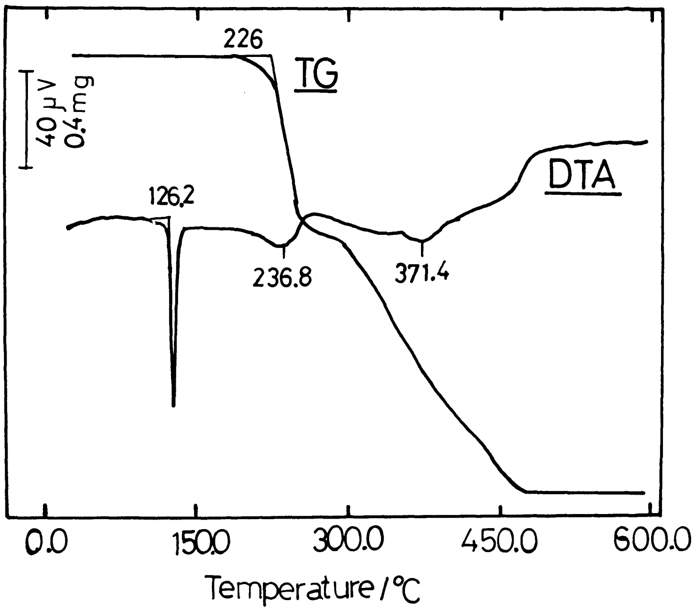


Fig. 1. DTA and TG curves of 1,6-bis(2-oxooxazolidine-3-ylcarbonylamino)hexane. Heating rate: 10 K min^{-1}

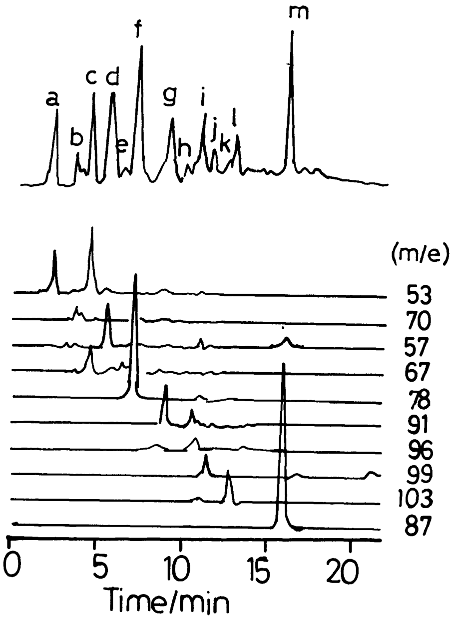


Fig. 2. Mass Chromatogram of the Decomposition products with TG-TRAP-GC/MS.

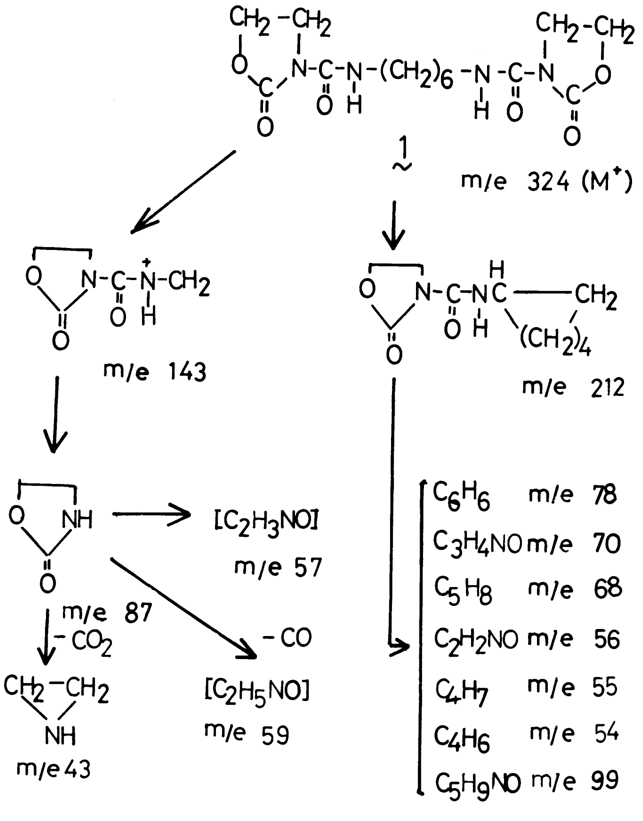
instruments, namely, TG, GC, and MS, in a Shimazu fasion as recently reported.[12)] Figure 2 shows a mass chromatogram of products of **1** obtained from this system. The thermally degraded products consist of a complex mixture of about 13 components.

Table 1. Mass spectral data for **1**

m/e[a)]	Relative intensity[b)]	Sigma(%)[c)]	Observed molecular weight	U.S.[e)]	Probable ion composition
43	34.72	5.05	43.0403 (43.0420)[d)]	1.0	C_2H_5N
56	13.35	1.94	56.0152 (56.0135)	2.5	C_2H_2NO
57	0.14	0.60	57.0216 (57.0213)	2.0	C_2H_3NO
59	36.19	5.26	59.0364 (59.0369)	1.0	C_2H_5NO
68	4.71	0.68	68.0648 (68.0624)	2.0	C_5H_8
70	13.39	1.94	70.0226 (70.0291)	2.5	C_3H_5NO
78	0.35	0.05	78.0500 (78.0469)	4.0	C_6H_6
87	66.99	9.75	87.0387 (87.0318)	2.0	$C_3H_5NO_2$
99	24.28	3.53	99.0692 (99.0681)	2.0	C_5H_9NO
143	100.00	14.55	143.0411 (143.0453)	3.5	$C_5H_7N_2O_3$
168	6.21	0.90	168.0880 (168.0894)	4.0	$C_8H_{12}N_2O_2$
212	1.16	0.17	212.1083 (212.1155)	4.0	$C_{10}H_{10}N_2O_3$
342	0.5	0.07	342.1486 (342.1530)	6.0	$C_{14}H_{22}N_4O_6$

a) Molecular ion is underlined.
b) Relative intensity reffered to base peak of spectrum as 100.
c) Peak hights expressed in per cent of total ionization.
d) Calculated values.
e) U.S.=Degree of unsaturation.

These components were readily identified by the mass spectrometer as listed in Table 1. This table tabulates m/e, its corresponding elemental composition, and the probable molecular structure of each of the identified components. The detailed mechanism of the cleavage is unknown at present. However, this mechanism suggests that the present cleavage also proceeds via the fragment ion (m/e 143) and the fragment ion (m/e 212) as represented in Scheme 1. The process at first involves the shifting of electrons. After the formation of the M$^+$ ion at m/e 342, the simple cleavage of a bond beta to the nitrogen atom of this ion leads to the species at m/e



Scheme 1.

143. After the loss of C_2H_2NO the cleavage stage follows to produce ion at m/e 87(oxazolidinone). This ion could lead to the species at m/e 59. The formation of the fragment ion at m/e 212 is the well-known McLafferty rearrangement process. This fragment ion splits into many species, such as m/e 99, 78, 70, 68, 56, 55, and 54. The fragment ion at m/e 87 is comparatively stable, since this ion was slower detected than the others. Further, from the first stage of weight loss in the TG curve this decomposing stage depended mainly on the generation of CO_2 gas. Since the other generated species were formed at the same time, it was suggested that the second stage of weight loss in the TG curve was related to the ejection of these species.

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