Thermal Behavior and Mass Spectra Aspects of 1,3,5-Triazine Derivatives Based on Isocyanuric Acid

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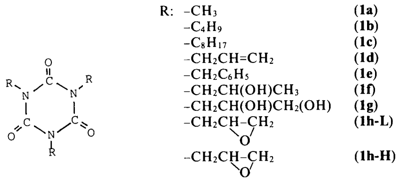
Synopsis. Eleven 1,3,5-triazine derivatives were investigated by the use of a thermal-analysis techniques. These compounds showed a remarkable difference in pyrolytic behavior and decomposed thermally by a cleavage of the triazine ring and the liberation of water, isocyanic acid, and carbondioxide. The pyrolysis products were separated and identified by a gas chromatograph coupled to a mass spectrometer. All of the obtained information led to the proposal of a thermal degradation mechanism for the triazine derivatives, which is presented here. The main pyrolysis and fragmentation by electron impact mechanisms were classified into four categories, respectively.

1,3,5-triazine derivaties have been widely used as the starting materials of resins or plastisizers. Detailed studies concerning the thermal decomposition process of these compounds have seldom been carried out. The results of several preliminary investigations have been reported.[1-3] In this paper the thermal behavior and

Table 1. Physical Properties of **1**



Compound	Elemental analysis (Calcd)/% C	H	N	Melting point/°C	Molecular weight	IR spectrum $\nu_{C=O}$
1a	42.11 (42.11)	5.37 (5.30)	24.66 (24.55)	79.5—90.2	171.16	1690
1b	60.78 (60.58)	9.16 (9.13)	14.04 (14.13)	Liquid	297.39	1690
1c	69.38 (69.64)	11.00 (11.01)	8.96 (9.02)	Liquid	465.70	1690
1d	57.64 (57.82)	6.33 (6.05)	16.67 (16.86)	Liquid	249.27	1700
1e	72.27 (72.17)	5.39 (5.30)	10.36 (10.52)	160.5—163.3	399.43	1690
1f	47.01 (47.52)	7.11 (6.98)	13.26 (13.85)	93.5—99.7	303.31	1690
1g	41.00 (41.03)	6.21 (6.03)	11.69 (11.69)	129.5—133.4	351.31	1690
1h-L	48.17 (48.49)	5.00 (5.09)	13.81 (14.14)	98.0—106.0	297.27	1690
1h-H	48.17 (48.49)	5.00 (5.09)	13.81 (14.14)	151.8—154.9	297.27	1690
1i	66.26 (66.25)	5.28 (5.56)	5.58 (8.58)	104.8—108.8	489.51	1690
1j	41.76 (42.10)	5.28 (5.30)	24.30 (24.55)	223.5—228.3	342.31	1675

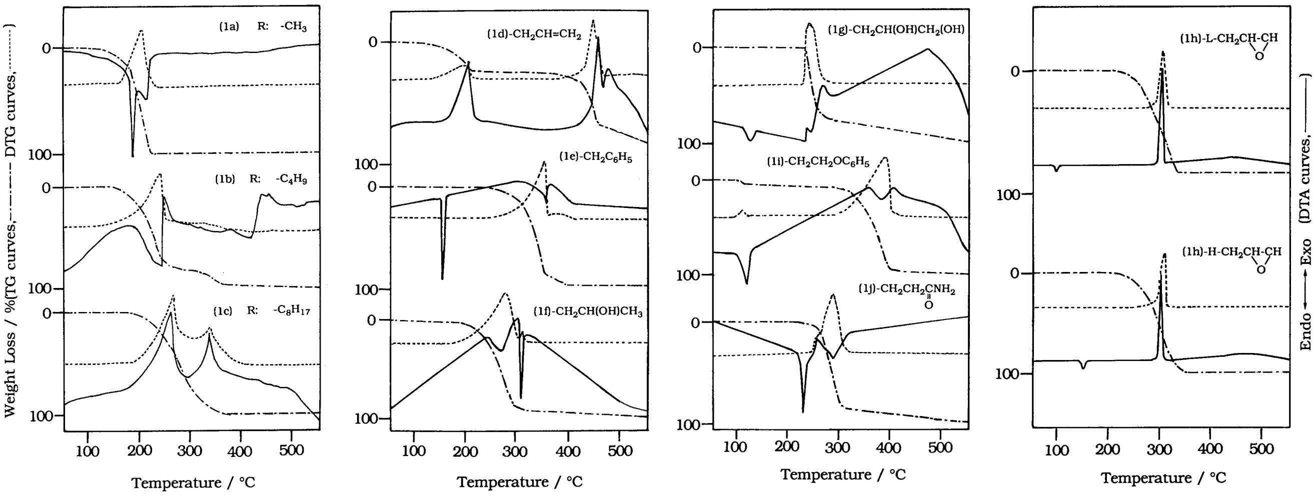


Fig. 1. DTA-TG/DTG curves of **1a**—**1j**.

products of the thermal degradation of derivatives, which have three side chains with various functional groups, are described.

Experimental

Materials. All of the derivatives studied were produced by Nissan Kagaku Co. Ltd. and used without further purification. Their physical properties are listed in Table 1.

Measurements. The elemental analyses were carried out using a Hitachi CHN Analyzer-026 at Toyama Medical and Pharmacy University. The IR spectra were recorded on a Nipponbunko IR-810 for a KBr disk or thin film between rock-salt plates. Electron-impact (EI) mass spectra were obtained on a JEOL-JMS-D300. Thermal analyses were carried out in air atmosphere using a Rigaku Denki THERMOFLEX TG-DTA 8112BH apparatus and a TAS100 system at various heating rates. Calcinated alumina was used as a reference material. TG-TRAP-GC/MS was carried out using a Shimadzu TGA-40 and a GC/MS-QP1000 combined system. An amount of 0.1—0.5 mg of the sample was pyrolysed at a heating rate of 10 °C min^{-1} in a helium atmosphere (flow rate: 50 ml min^{-1}) using a quartz tube. The volatile products formed during pyrolysis were collected in a trap cooled with liquid nitrogen and then introduced into a gas chromatograph-mass spectrometer. Column: OV-17, Glass spiral, chromosorb W 80—100 mesh (Shimadzu). The initial column temperature was kept at 50 °C, then heated to 230 °C at 5 °C min^{-1}. and allowed to stay at 230 °C for 4 min. The energy of ionizing electrons was 20 eV.

Results and Discussion

The DTA-TG-DTG curves of **1a**—**1j** are shown in Fig. 1. In the case of **1a**, two endothermic peaks are observed in the DTA curve. The first narrow peak may be attributed to the sublimation of **1a**, since this peak is not due to the melting of material, and there is no endothermic peak at the melting point. Since the two peaks overlap, the sublimation and thermal decomposition of **1a** probably occur simultaneously. The derivatives of **1a**, **1e**, **1f**, and [**1h-L**]—**1j** are pyrolyzed in one stage, **1b**, **1c**, and **1g** in two stages, and **1d** in three stages. As can be seen from their DTA curves, however, the pyrolysis processes of **1f** and **1g** are complex. The activation energies of thermal decomposition were calculated for 8 derivatives using the Ozawa method.[4] These data are listed in Table 2. In the case of **1a**, **1b**, and **1c**, in which the side chains are normal alkyl groups, the activation energies increased with increasing the length of their side chains. In practice, however, the value of **1a** is higher than that of **1b**. For this reason, **1a** may be sublimated as described proviously; hence, the activation energy of **1a** becomes greater. Further, in the case of **1f** and **1g**, the activation energy is affected by a hydroxyl group of the side chain.

The cleavage mechanism by electron impact for **1a**—**1j** was investigated by high-resolution mass spectroscopy. Table 3 shows the mass spectral data (EI method) and TG-TRAP-GC/MS for **1a**—**1j**. The cleavage mechanism by electron impact of their materials were classified into the following four categories: 1) Two hydrogen atoms are rearranged to a nitrogen atom in the triazine ring from one of the three side chains, and a triazine ring is opened at the neighborhood of this nitrogen atom. Then, the remaining two side chains are cleaved. Derivatives **1b**, **1c**, and **1g** belong to this classification. 2) It is observed that elimination of the side chain occurs from the triazine ring without a rearrangement of the side chain to the nitrogen atom of the ring; the ring then cleaves simply. Compounds **1d** and **1e** fell under this category. 3) It is found that the cleavage or elimination of the side chain takes place with the elimination of radicals. Fragment ions which have ethyl or vinyl groups in the side chains are observed with strong intensity. Compounds **1f**—**1j** were classified into this category. 4) Cleavage of the side chain and the triazine ring occurred at the same time. The cleavage mechanism belongs to neither of the above three classifications. Compound **1a** fell under this category. The products of pyrolysis were identified by TG-TRAP-GC/MS. Furthermore, the results obtained from this method were compared with the EI-mass spectra of the same compounds. Table 3 also shows a gas chromatogram of the thermal decomposition products of **1a**—**1j**. In the case of the thermal decomposition of **1c**, about six major products were separated by gas chromatography. Peaks Nos. 1 and 2 are attributed to carbon dioxide (m/z 44) and moisture on the sample (m/z 18), respectively. Peaks Nos. 3, 4, and 5 may all be due to the thermal degradation products derived from the side chains of **1c**. These products are assumed to be an alkene by interpretation of their mass spectra. Peak No. 6 may be attributed to octyl isocyanate. In comparison with the EI mass spectrum, the only fragment ions derived from the side chain and octyl isocynate are observed in the case of pyrolysis, while in the EI method the fragment ions corresponding to high mass number are principally observed. The above results and data of the thermal decomposition process for the eleven derivatives were classified into the following four modes:. 1) As the result of a simple cleavage of the triazine ring, isocyanate was formed. Derivatives **1b**—**1g** belong to this mode. 2) The side chain was eliminated from the triazine ring with hydrogen rearrangements; consequently, the pyrolysis products arising from this process and from isocyanic acid were formed. Derivatives **1h-L**, **1h-H**, and **1j** were classified into this category.[5] 3) The side

Table 2. Activation Energies in a Thermal Decomposition for (**1a**—**1j**)

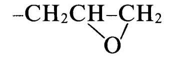
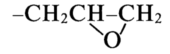
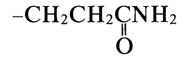
Compound	Substituent	E_a/kJ mol^{-1}
(**1a**)	$-CH_3$	114
(**1b**)	$-C_4H_9$	83
(**1c**)	$-C_8H_{17}$	132
(**1d**)	$-CH_2CH=CH_2$	—
(**1e**)	$-CH_2C_6H_5$	123
(**1f**)	$-CH_2CH(OH)CH_3$	128
(**1g**)	$-CH_2CH(OH)CH_2(OH)$	109
(**1h-L**)	 $-CH_2\underset{\diagdown O \diagup}{CH-CH_2}$	—
(**1h-H**)	 $-CH_2\underset{\diagdown O \diagup}{CH-CH_2}$	—
(**1i**)	$-CH_2CH_2OC_6H_5$	124
(**1j**)	 $-CH_2CH_2\underset{\underset{O}{\parallel}}{C}NH_2$	108

Table 3. Mass Spectral and Mass Chromatogram Data for **1a**—**1j**

Mass Spectral Data (EI method)				TG-TRAP-GC/MS		
Compound	m/z	Sigma / %	Probable ion composition	Peak No.[a)]	Retention time/min^{-1}	m/z
1a	58	21.45	C_2H_4NO	1	1.7	44
	143	8.51	$C_4H_5N_3O_3$	2	2.0	18
	171	42.28	$C_6H_9N_3O_3$	3	23.9	217
1b	70	4.24	C_3H_4NO	1	1.6	44
	186	4.70	$C_7H_{12}N_3O_3$	2	2.2	40, 54, 56
	200	5.34	$C_8H_{14}N_3O_3$	3	7.8	18, 43
	242	48.69	$C_{11}H_{20}N_3O_3$			
	297	4.52	$C_{15}H_{27}N_3O_3$			
1c	256	5.28	$C_{12}H_{22}N_3O_3$	1	1.7	44
	354	62.92	$C_{19}H_{36}N_3O_3$	2	2.1	18
	408	2.21	$C_{23}H_{42}N_3O_3$	3	2.3	18, 43
	465	5.38	$C_{27}H_{51}N_3O_3$	4	3.2	18, 26, 28, 53
				5	6.2	18, 28, 41, 42, 43, 55, 56, 69, 70
				6	12.5	85, 98, 99
1d	83	24.43	C_4H_5NO	1	3.0	28, 54, 55, 56
	125	4.86	$C_5H_5N_2O_2$	2	10.3	41, 58, 100
	208	4.60	$C_9H_{10}N_3O_3$	3	13.1	44, 72
	249	30.97	$C_{12}H_{15}N_3O_3$	4	14.6	41, 56, 68, 73, 82
				5	16.7	217
				6	17.5	204, 217
				7	18.5	103, 217
				8	22.6	82, 83, 84
1e	91	5.48	C_7H_7	1	2.2	18
	132	9.61	C_8H_6NO	2	8.0	18, 91, 106
	175	28.18	$C_9H_7N_2O_2$	3	10.2	18, 105, 106
	308	4.44	$C_{17}H_{14}N_3O_3$	4	13.2	18, 133
	399	32.79	$C_{24}H_{21}N_3O_3$			
1f	83	4.02	C_4H_5NO	1	2.1	18, 29, 43, 44
	84	4.23	C_4H_6NO	2	2.5	18, 28, 29, 43, 58, 75
	183	5.59	$C_7H_9N_3O_3$			
	223	8.39	$C_{10}H_{13}N_3O_4$			
	241	23.96	$C_{10}H_{15}N_3O_4$			
	259	15.36	$C_{10}H_{17}N_3O_5$			
1g	86	2.22	$C_3H_4NO_2$	1	1.4	43, 44
	143	4.51	$C_4H_6NO_2$	2	3.5	18, 27, 28, 55, 56
	172	4.70	$C_5H_6N_3O_4$	3	13.5	18
	199	1.79	$C_7H_9N_3O_4$			
	228	2.63	$C_8H_{10}N_3O_5$			
	273	7.74	$C_{10}H_{15}N_3O_6$			
	278	11.41	$C_9H_{16}N_3O_7$			
	291	6.29	$C_{10}H_{17}N_3O_7$			
	302	9.74	$C_{11}H_{16}N_3O_7$			
	320	4.88	$C_{11}H_{18}N_3O_8$			
1h	56	6.24	C_3H_4O	1	1.8	44
	70	3.59	C_2NO_2	2	2.3	18
	82	5.00	C_4H_4NO	3	2.7	18, 43
	99	5.31	$C_3H_3N_2O_2$	4	3.6	27, 28, 55, 56
	130	2.15	$C_3H_4N_3O_3$			
	143	3.88	$C_4H_5N_3O_3$			
	157	3.29	$C_5H_7N_3O_3$			
	185	2.07	$C_7H_{11}N_3O_3$			
	213	4.80	$C_8H_{11}N_3O_4$			
	255	4.52	$C_{10}H_{13}N_3O_5$			
	267	2.68	$C_{11}H_{13}N_3O_5$			
	269	4.40	$C_{11}H_{15}N_3O_5$			
1i	121	2.83	C_8H_9O	1	1.5	28, 44
	182	5.03	$C_7H_8N_3O_3$	2	4.8	91, 107
	276	6.77	$C_{13}H_{14}N_3O_4$	3	8.7	28, 32, 94, 95
	396	52.18	$C_{21}H_{22}N_3O_5$			
1j	44	6.09	CH_2NO	1	2.0	17, 18
	71	15.42	C_3H_5NO	2	2.1	18, 43
	155	6.32	$C_5H_5N_3O_3$	3	2.5	26, 43, 52, 53
	183	2.63	$C_7H_9N_3O_3$	4	10.1	55, 71

a) Mass chromatogram of the decomposition products.

chain cleaved. This manner was found in the pyrolysis process of **1b**, **1c**, **1f**, **1g**, and **1i**. 4) Sublimation or/and gasification with pyrolysis occurred. Compounds **1a** and **1d** fell under this category.

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