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THE EFFECT OF TRIETHANOLAMINE ON THERMAL DECOMPOSITION OF GAP

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ABSTRACT

The effect of triethanolamine (TEA) on thermal behavior of glycidyl azide polymer (GAP) has been investigated by direct pyrolysis mass spectrometry technique. It has been observed that thermal degradation of GAP-TEA mixture also begins with the cleavage of the side groups as in the case of GAP. Again, the main decomposition started with the elimination of molecular nitrogen from the azide functional group, and a quite similar degradation mechanism has been proposed. The increase in the thermal stability of GAP in the presence of TEA was attributed to formation of a crosslinked structure. The heating rate had little impact on the relative abundances of the degradation products of the GAP-TEA mixture contrary to what has been observed for GAP. Thus, it may be proposed that the effect of heating rate on thermal degradation behavior of a crosslinked polymer is negligible.

Key Words: GAP; Pyrolysis mass spectrometry; Triethanolamine; Thermal degradation

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INTRODUCTION

Glycidyl azide polymer, GAP, is among the most widely used binders that act as a fuel in solid composite propellants. Thus, several studies on thermal degradation of GAP have been appeared in the literature.^[1–9]

It has been observed that the decomposition of GAP starts with the elimination of molecular nitrogen from the azide group, with the initial rupture of N-N₂ bond.^[1–9] Rearrangement reactions and/or H₂ evolution after the initiation step result in various polymeric structures that decompose subsequently.^[4,9] Depolymerization type reactions and loss of low molecular weight species such as N₃, HN₃, CH₂N₃ and CH₃N₃ have also shown to be effective.^[4] Final gaseous products of decomposition include N₂, CO, HCN, NH₃, CH₂O, CH₄ and C₂H₂.^[4–9] Relatively large molecules, such as benzene, pyrrole, furan and nitrogen containing polyatomic molecules, have also been identified.^[4]

Actually, the thermal performance and the burning rate characteristics of composite propellants depend not only on the fuel but also on the composition of the propellant. The objective of this work is to investigate the effect of triethanolamine, TEA, a widely used bonding agent in solid composite propellants, on the thermal behavior of GAP by direct pyrolysis mass spectrometry technique.^[9–11] Effect of heating rate on thermal decomposition has also been studied.

EXPERIMENTAL

GAP was purchased from 3M Company. Its density is 1.3 g/mL and viscosity at 25°C is 5000 cps. Triethanolamine TEA was purchased from Merk KgaA. The ratio of TEA to binder in the mixtures was adjusted to 1/150.

Direct insertion probe pyrolysis mass spectrometry system used for thermal analyses consists of a 5973 HP quadruple mass spectrometry coupled to a SIS direct insertion probe. The maximum attainable temperature is 445°C. Mass spectra of the products were recorded at a scan rate of 2 scans/s in the mass range of 10–700 amu using 70 and 19 eV electrons. Two different heating rates, namely 10°C/min or 900°C/min, have been applied to investigate the effect of heating rate on the thermal degradation behavior.

RESULTS AND DISCUSSIONS

The direct insertion probe pyrolysis mass spectrometry results for GAP and GAP-TEA mixture obtained at a heating rate of 10°C/min were in accordance with the TGA results indicating that the main decomposition

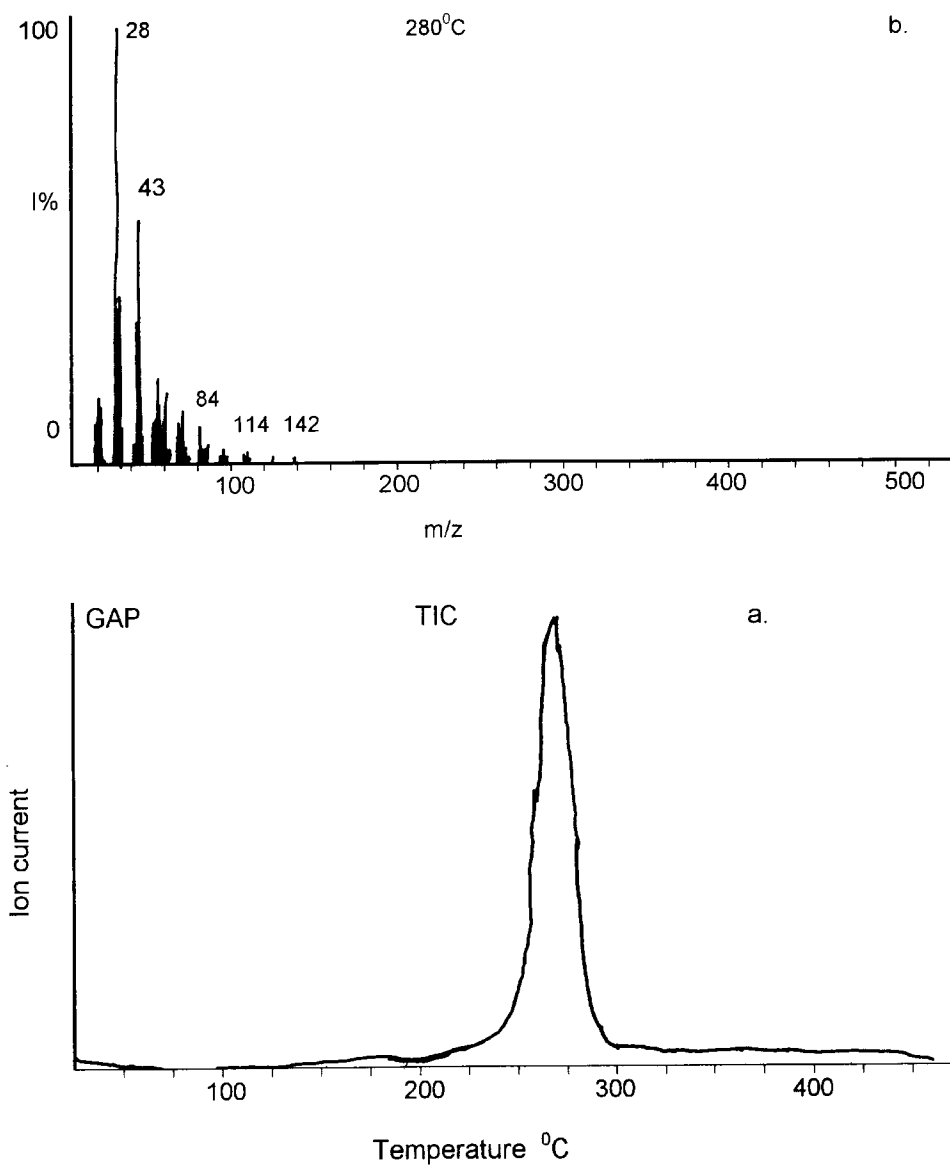


Figure 1. a. The TIC curve of GAP, and b. the pyrolysis mass spectrum recorded at the maximum of TIC curve.

occurs above 260°C in a single step. The total ion current, TIC, curves of pure GAP and GAP-TEA mixture are shown in Figs. 1 and 2, respectively. An intense sharp peak is present in the TIC curve of the mixture at initial stages of heating (Fig. 2a). The analysis of the mass spectra recorded at this stage showed diagnostic peaks of TEA; the molecular ion peak at m/z 149, base peak at m/z 118 due to loss of CH_2OH group, and intense peaks at

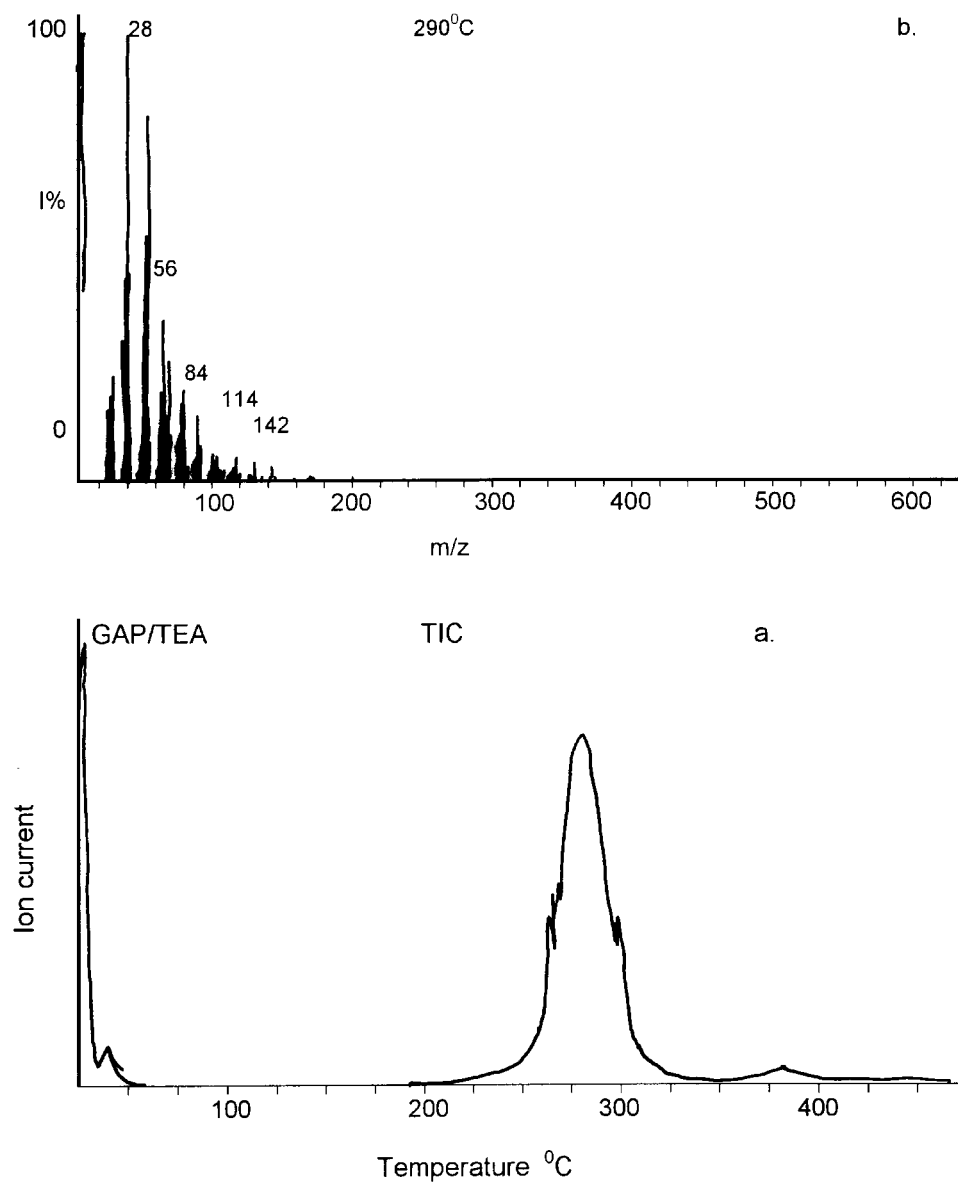


Figure 2. a. The TIC curve of GAP-TEA mixture, and b. the pyrolysis mass spectrum recorded at the maximum of TIC curve.

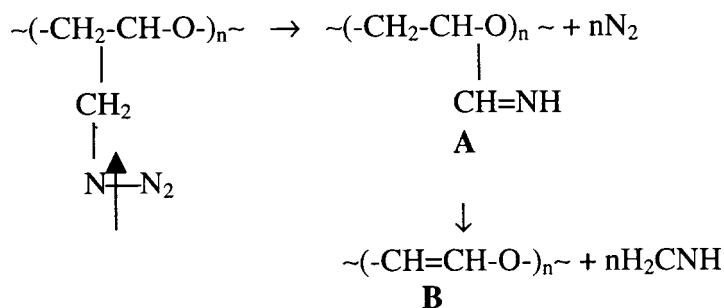
m/z 74, due to $\text{NHCH}_2(\text{C}_2\text{H}_4\text{OH})$, at m/z 56 due to $\text{NCH}_2(\text{C}_2\text{H}_4)$, at m/z 45 due to $\text{C}_2\text{H}_4\text{OH}$, at m/z 31 due to CH_2OH and at m/z 28 attributed to both C_2H_4 and NCH_2 . Thus, evolution of TEA at initial stages was confirmed. For both the GAP and GAP-TEA mixtures, the main degradation occurred above 250°C . Yet, it can be noted from Figs. 1 and 2 in the presence of TEA,

Table 1. Relative Intensities of Characteristic Peaks in the Pyrolysis Mass Spectra of GAP and GAP-TEA Mixture During Thermal Decomposition at a Heating Rate of 10°C/min

m/z	GAP 280°C	GAP-TEA 290°C	Assignments
26	218	352	C ₂ H ₂ , CN
27	1442	2494	HCN
28	10000	10000	N ₂ , CO, C ₂ H ₄
42	3259	5543	B, CH=CHO
43	5582	8236	C ₂ H ₃ O, HN ₃
44	3199	6634	E, CH ₂ CH ₂ O
56	2053	3718	D, CH ₂ C(CH ₂)O
57	2114	2114	CH ₂ CH(CH ₂)O
69	612	1167	C, CH ₂ CH(CN)O
71	670	1244	A, CH ₂ CH(CH=NH)O
84	893	1659	Dimer of B
88	150	269	Dimer of E
99	230	438	Monomer of GAP
112	134	245	Dimer of D
126	90	150	Trimer of B
132	59	102	Trimer of E
138	38	58	Dimer of C
142	169	308	Dimer of A
168	24	47	Tetramer of B, Trimer of D
176	13	21	Tetramer of E
198	16	37	Dimer of GAP
207	5	8	Trimer of C
210	10	12	Pentamer of B
213	20	34	Trimer of A
224	7	12	Tetramer of D
252	4	5	Hexamer of B
297	4	5	Trimer of GAP

decomposition of GAP occurred in a broader and slightly higher temperature range. The mass spectra recorded at TIC maxima, at 280°C for GAP and 290°C for GAP-TEA mixture are given in Figs. 1b and 2b, and the related data are collected in Table 1.

In a recent publication, we discussed the thermal degradation mechanism of GAP in detail and determined that the azide rupture reaction is the main initiation step for the thermal decomposition of GAP as proposed in the literature.^[1-9] Yet, our results also indicated that a depolymerization type mechanism yielding mainly the monomer and low molecular weight oligomers should also be taken into consideration.^[9] Furthermore, various polymeric structures (A, B, C, D, E) as a result of rearrangement reactions and/or H₂ evolution after the initiation step, as summarized in Schs. 1-5, were identified.

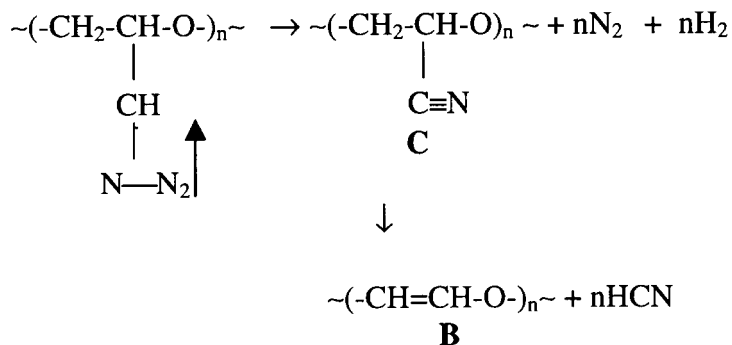


Scheme 1.

The evolution of degradation products continued in the high temperature ranges for both GAP and GAP-TEA mixture and was associated with decomposition of the various polymeric structures produced (A, B, C, C ,D, E) in the initiation step.

The pyrolysis mass spectral data indicated that in the presence of TEA the relative intensities of all fragment peaks increased with respect to the base peak at m/z 28 mainly due to evolution of N_2 (Table 1). The direct elimination of N_2 was somehow depressed in the mixture. Thus, it may be proposed that triethanolamine acted as a crosslinking agent and increased the thermal stability of GAP suppressing the evolution of N_2 .

Application of a ballistic heating rate ($900^\circ\text{C}/\text{min}$) yielded pronounced differences in the TIC curves. In Fig. 3-a and b the TIC curves of GAP and GAP-TEA mixture are shown respectively. Two peaks are present in the TIC curve of GAP. Whereas, in the TIC curve of the mixture, a broad peak with some structure is observed after a slightly longer period of time. This behavior indicates an increase in thermal stability of the polymer, GAP in the presence of TEA. The intense and/or characteristic peaks present in the mass spectra recorded at the maxima of the TIC curves are collected in Table 2.



Scheme 2.

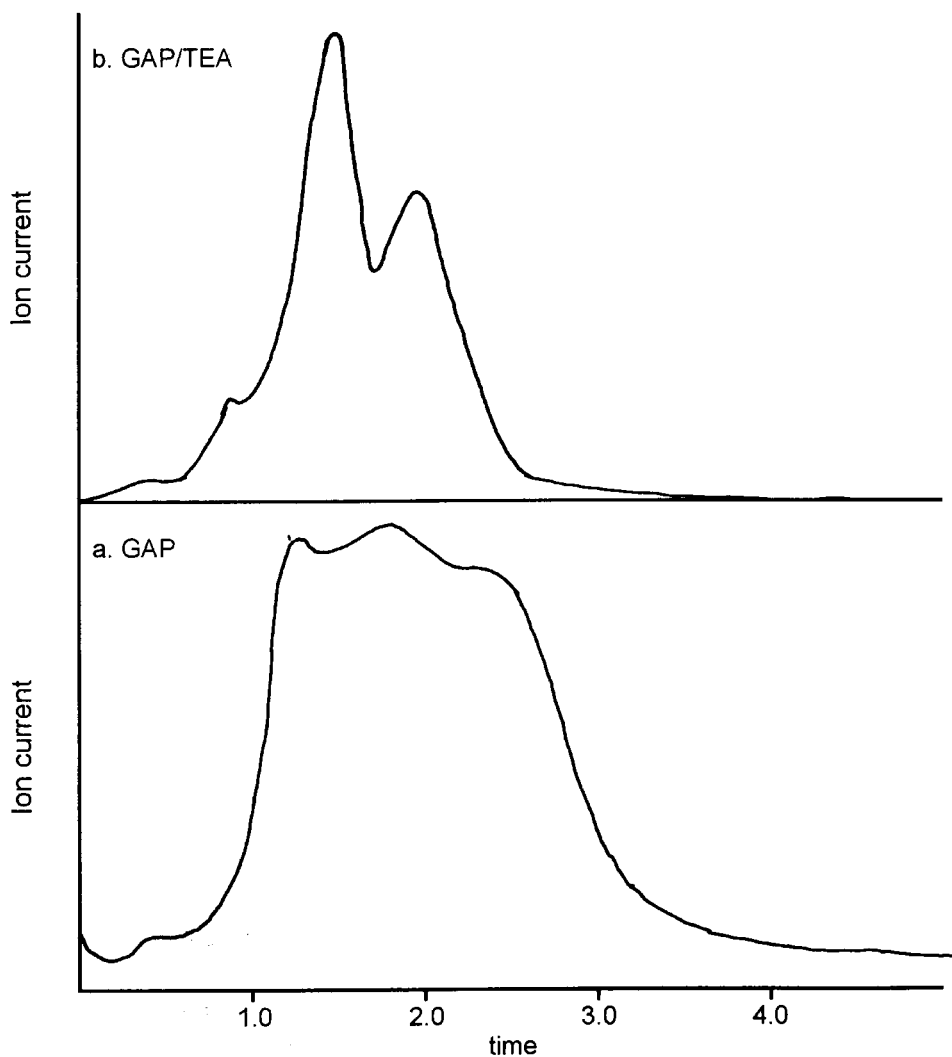


Figure 3. The TIC curves of a. GAP, and b. GAP-TEA mixture, recorded during pyrolysis at a heating rate of 900°C/min.

CONCLUSION

The effect of triethanolamine on thermal behavior of GAP has been investigated by direct pyrolysis mass spectrometry technique. The thermal decomposition of GAP-TEA mixture also begins with the evolution of molecular nitrogen from the azide functional group. Various polymeric structures formed in the initial degradation stage decompose subsequently as in the case of GAP. It has been determined that the thermal stability of GAP

Table 2. Relative Intensities of Characteristic Peaks in the Pyrolysis Mass Spectra of GAP and GAP-TEA Mixture During Thermal Decomposition at a Heating Rate of 900°C/min

m/z	GAP		GAP-TEA			Assignments
	1.5 min	2.25	1.4	1.9	2.6	
28	10000	10000	1000	1000	1000	N ₂ , CO, C ₂ H ₂
42	6132	4579	4047	4639	3604	B, CH=CHO
44	7054	5671	5275	4902	5628	E, CH ₂ CH ₂ O
56	4808	3371	3479	4115	2612	D, CH ₂ C(CH ₂)O
69	1907	1345	1398	1709	1017	C, CH ₂ CH(CN)O
71	1980	1178	1532	1745	956	A, CH ₂ CH(CH=NH)O
84	3081	1799	2045	2428	1254	Dimer of B
88	505	264	306	369	189	Dimer of E
99	1043	612	617	825	426	Monomer of GAP
112	816	487	434	623	326	Dimer of E
126	559	364	270	432	240	Trimer of B
132	318	222	145	228	136	Trimer of E
138	311	199	119	257	130	Dimer of C
142	1086	450	487	532	253	Dimer of A
168	246	162	80	163	95	Tetramer of B, Trimer
176	78	102	37	85	0	Tetramer of E
198	152	107	48	97	63	Dimer of GAP
207	72	53	21	48	33	Trimer of C
210	115	75	28	73	43	Pentamer of B
213	247	133	76	126	71	Trimer of A
220	25	43	12	32	23	Pentamer of E
224	105	74	27	59	36	Tetramer of D
252	72	43	16	41	22	Hexamer of B
264	29	31	9	25	15	Hexamer of E
276	21	18	5	13	10	Tetramer of C
280	48	25	11	26	16	Pentamer of D
284	125	50	34	52	23	Tetramer of A
294	38	27	9	20	12	Heptamer of B
297	63	29	14	29	13	Trimer of GAP
308	2	19	7	17	9	Heptamer of E
345	8	8	3	9	4	Pentamer of C
355	33	18	10	19	4	Pentamer of A
396	32	8	5	13	5	Tetramer of GAP
426	22	10		8	3	Hexamer of A
495	8	5	4	5	1	Pentamer of GAP

increases in the presence of TEA indicating formation of a crosslinked structure. Furthermore, it has been noted that the heating rate has negligible effect on the relative abundances of degradation products of the mixture. This behavior points out that the heating rate has little impact on thermal decomposition products of a crosslinked polymer.

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