Primary Pyrolysis Products of Hydroxy-Terminated Polybutadiene

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ABSTRACT: This is the first report on the analysis of primary degradation products of a widely used commercial propellant binder, viz. hydroxy-terminated polybutadiene (HTPB), which has been carried out by direct pyrolysis mass spectrometry. The mechanism of degradation involves a radical process forming cyclic compounds as well as β-CH transfer reactions to form linear oligomers. On the basis of heats of formation data, it was found that the formation of 1,3-butadiene monomer is not favored during the primary chain scission process. However, its formation appears to emanate from the dissociation of high molecular weight cyclics/linear oligomers. In the presence of strong oxidizers such as ammonium perchlorate, the degradation pattern of HTPB, as observed in pyrolysis−gas chromatography/mass spectrometry analysis, is significantly affected, indicating its influence on HTPB degradation.

Introduction

Hydroxy-terminated polybutadiene (HTPB) is a widely used fuel binder in composite solid propellants all over the world.[1,2] Besides, it also finds applications in adhesives and sealants, etc. The major ingredients of composite solid propellants are ammonium perchlorate (AP) and HTPB.[1] While the thermal decomposition and combustion of AP have been widely studied,[3] on the other hand, for the same characteristics HTPB has not been explored much.[4−6] Understanding the degradation mechanism of HTPB is necessary from the viewpoint of knowing not only the complex combustion behavior of the propellant but also its aging phenomenon.

Earlier studies on the analysis of the degradation products of HTPB using the pyrolysis−gas chromatography/mass spectrometry (Py-GC/MS) method provided information only on the secondary degradation products.[7] Hitherto no studies are available on the primary degradation mechanism of HTPB which is of considerable interest in determining the initial bond breakage reactions. To gain insight into the primary degradation process, in the present study, we have carried out the direct pyrolysis mass spectrometric (DPMS) analysis of HTPB wherein the sample is pyrolyzed very close to the ion source, and the primary chain cleavage products are immediately driven to the detector for obtaining the mass spectra.[8−15] In addition, we have also performed a detailed Py-GC/MS analysis of HTPB to compare the secondary products formed by this method mechanistically with the primary products obtained from the DPMS analysis.

It is well-known that the oxidizer AP considerably influences the degradation behavior of the binder. To find out as to how AP influences HTPB degradation, we have also performed both DPMS and Py-GC/MS analysis of HTPB in the presence of AP. It is hoped that these studies would be useful in providing a clearer understanding of HTPB degradation under combustion conditions.

Experimental Section

HTPB and AP were obtained from Vikram Sarabhai Space Centre, Trivandrum, and were used without further purification.

Preparation of HTPB/AP Mixtures. An 80 mg sample of HTPB and 20 mg of AP were physically mixed to get the blend of HTPB/AP (80/20). Other compositions were also prepared in a similar fashion.

Thermogravimetry. A Perkin-Elmer thermal analyzer, TGS-2, was used to determine the thermal stability of the polymers. Experiments were carried out using 2 mg of sample, under nitrogen, at a heating rate of 10 °C/min.

DPMS. Pyrolysis was carried out using the direct insertion probe of a VG MICRO-MASS 7070H mass spectrometer, heated from 50 to 500 °C at a heating rate of 32 °C/min. Electron ionization (EI) was maintained at 18 eV, and chemical ionization (CI) was performed with methane as the reagent gas.

Pyrolysis-GC/MS. Flash pyrolysis experiments were carried out using a Curie-point pyrolysis unit directly connected to the injector of a Hewlett-Packard 5890 gas chromatograph. The on-line flash pyrolysis experiments were performed by inductive heating of the sample-coated wires at 700 °C. The separated products were analyzed by the mass spectrometer.

Results and Discussion

Thermogravimetry. The dynamic TG and DTG of neat HTPB and its mixture with AP are presented in Figures 1 and 2, respectively. Figure 1 clearly reveals that the onset of thermal degradation of HTPB gets shifted to lower temperatures in the presence of AP. Further, it shows two-step degradation. The data on the onset temperature (T_i), peak temperature (T_m), final temperature (T_f) of degradation, and also percentage weight loss are presented in Table 1. It is interesting to note that the percentage weight loss of stage I increases with the AP concentration in the mixture. This

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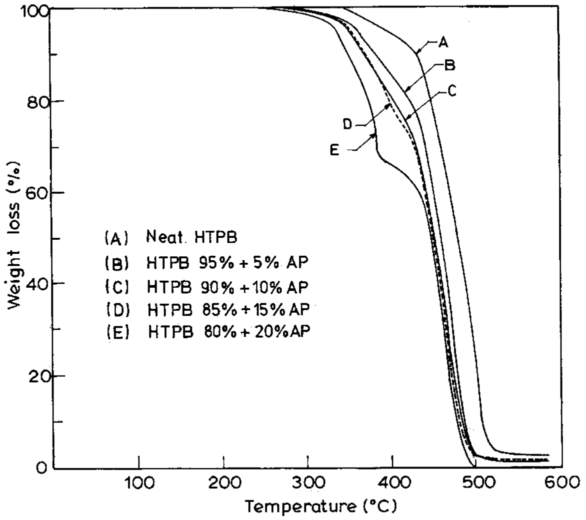


Figure 1. TGA traces of neat HTPB and HTPB/AP mixtures.

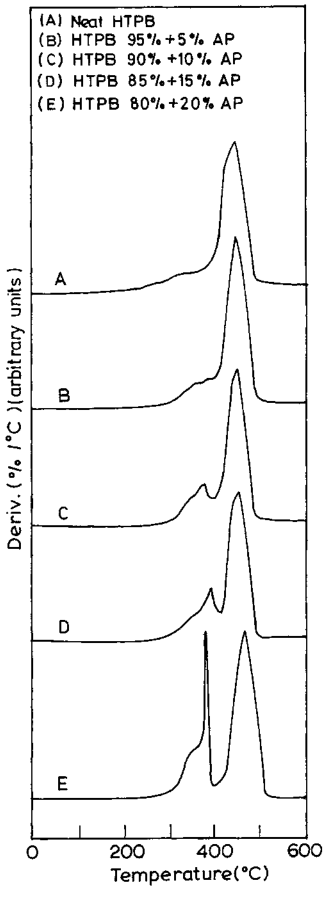


Figure 2. DTG traces of neat HTPB and HTPB/AP mixtures.

suggests that considerable interaction is occurring between HTPB and AP in the condensed phase.

DPMS. The EI and methane CI mass spectra of HTPB are shown in Figure 3, a and b, respectively. The structural assignments of the molecular ions appearing in both mass spectra are given in Table 2. It could be noted here that, apart from cyclic compounds and linear oligomers, we also observe low molecular weight species such as 1,3-butadiene and 2-pentene. The primary products (Table 2) can originate from various types of chain scission reactions, as shown in Scheme 1. The degradation is initiated both by the breakage of the C−C bond β to the double bond followed by cyclization, as well as β-CH hydrogen transfer reactions forming linear oligomers. Formation of 4-vinylcylohexene is attributed to the 1,2-structures present in the backbone.

Table 1. Thermal Data for the Decomposition of HTPB and (HTPB/AP)[a]

sample (wt % AP)	T_i (°C)	T_m (°C)	T_f (°C)	wt loss (%)
neat HTPB	330 (F)	377 (F)	395 (F)	7.92 (F)
	395 (S)	471 (S)	505 (S)	88.3 (S)
A (5)	330 (F)	374 (F)	410 (F)	15.7 (F)
	415 (S)	471 (S)	505 (S)	79.4 (S)
B (10)	325 (F)	386 (F)	415 (F)	22.7 (F)
	415 (S)	467 (S)	500 (S)	73.4 (S)
C (15)	320 (F)	399 (F)	420 (F)	26.1 (F)
	420 (S)	463 (S)	510 (S)	69.8 (S)
D (20)	315 (F)	384 (F)	400 (F)	31.7 (F)
	400 (S)	471 (S)	495 (S)	64.3 (S)

[a] T_i = initial decomposition temperature; T_m = peak decomposition temperature; and T_f = final decomposition temperature. F = first stage and S = second stage.

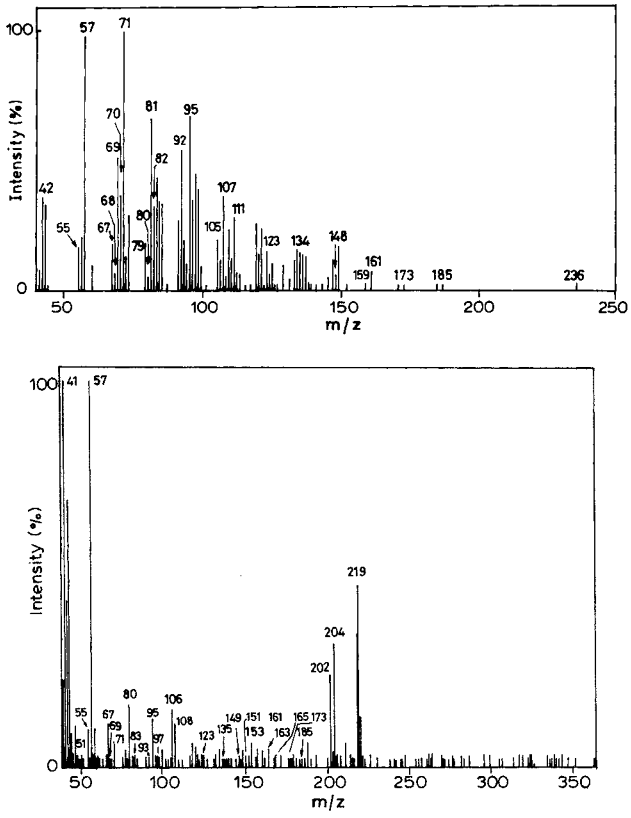
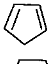
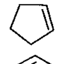
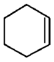
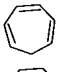
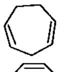
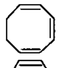
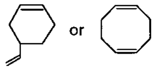
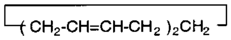
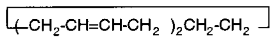
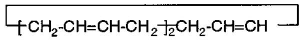
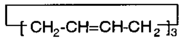
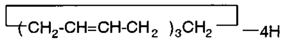
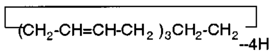


Figure 3. DPMS of HTPB: (a, top) EI and (b, bottom) methane CI.

Thermochemistry of Cyclization vs Unzipping. To substantiate the mechanism of degradation, we have carried out thermochemical calculations which is primarily based on the heats of formation (ΔH_f°) data.[16,17] We have considered here three possible model reactions which could yield only butadiene (eq 1) or cyclics (eq 2) or butadiene + cyclics (eq 3) from the same backbone unit (see Table 3). Comparing the heats of degradation (ΔH_d°) of the three reactions, it appears that the most preferred pathway of HTPB degradation is the formation of cyclics (eq 2) and the least favored is the formation of 1,3-butadiene (eq 1). This would mean that 1,3-butadiene detection in the DPMS analysis could possibly be due to the degradation of thermally unstable cyclic or linear oligomers (Scheme 1).

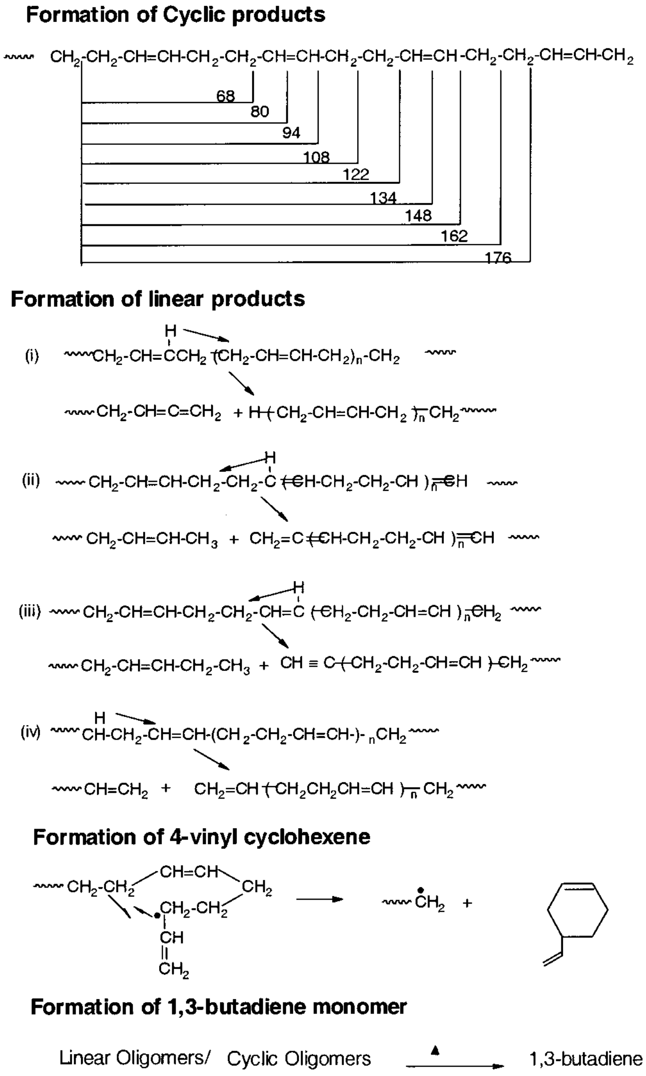
Table 2. Primary Degradation Products Observed in the DPMS of HTPB

Compounds	m/z
$CH_2=CH-CH=CH_2$	54
$CH_3-CH=CH-CH_2-CH_3$	70
	66
	68
	78
	80
	82
	92
	94
	106
 or	108
 $(CH_2-CH=CH-CH_2)_2CH_2$	122
 $(CH_2-CH=CH-CH_2)_2CH_2-CH_2$	134
 $[CH_2-CH=CH-CH_2]_2CH_2-CH=CH$	148
 $[CH_2-CH=CH-CH_2]_3$	162
 $(CH_2-CH=CH-CH_2)_3CH_2$ —4H	172
 $(CH_2-CH=CH-CH_2)_3CH_2-CH_2$ --4H	184
$CH_3(CH=CH-CH_2-CH_2)_nC\equiv CH$	40(0), 202(3)
$CH_3(CH_2-CH_2-CH=CH)_nCH=CH_2$	42(0), 96(1), 150(2), 204(3)
$CH\equiv C(CH_2-CH=CH-CH_2)_nC\equiv CH$	50(0), 104(1), 158(2),
$CH_2=C(=CH-CH_2-CH_2-CH=)_nC=CH_2$	52(0), 160(2)
$H(CH_2-CH=CH-CH_2)_nH$	56(1), 110(2), 164(2), 218(3)

Flash Pyrolysis GC/MS of HTPB. The Py-GC/MS pyrogram of neat HTPB is shown in Figure 4, and the products formed are displayed in Table 4. Here the base peak is 1,3-butadiene, and the other major products are cyclic compounds. Py-GC/MS results significantly match with the DPMS data except for the linear oligomers which are absent in the Py-GC/MS experiment due to their thermal instability. Very high concentrations of cyclic compounds in the Py-GC/MS analysis revealed that in HTPB degradation formation of cyclics is most favored.

It may be noted that Py-GC/MS of neat HTPB has been reported earlier.[7] Unlike a wide distribution of products observed in the present study, the earlier report[7] by Du found only a few products, namely, 1,3-butadiene, cyclopentene, cyclohexadiene, and 4-vinylcyclohexene. Although these products are formed in the present study as well, a very large difference in the product spectrum could be due to the poor resolution of the instrument in the earlier studies. Du[7] also reported that 1,3-butadiene formation occurs on account of depolymerization reactions. But, our studies indicate that the 1,3-butadiene monomer may come from the degradation of either cyclic or linear oligomers rather than from direct unzipping of the HTPB chain.

Scheme 1. Thermal Degradation Mechanism of HTPB

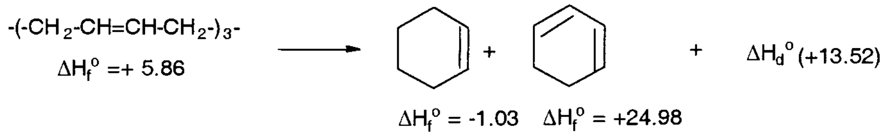


Interaction of AP with HTPB. It is reported that the C=C bond of HTPB backbone gets very easily oxidized.[18] To analyze as to how the strong oxidizer like AP influences the HTPB degradation, a mixture of HTPB/AP (80/20) was subjected to DPMS analysis (spectrum not reported here for brevity).The DPMS of HTPB/AP (80/20) was very similar to the neat HTPB, indicating that AP does not influence the primary degradation mechanism of HTPB under DPMS mode.

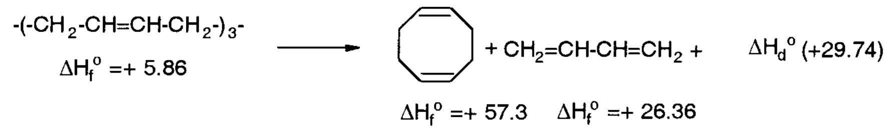
The Py-GC/MS pyrogram of HTPB/AP (80/20) mixture is given in Figure 5, and the structures of the products formed are presented in Table 4. On comparing with neat HTPB pyrogram (Figure 4), here 1,3-cyclohexadiene forms the base peak; besides, we also observe oxidized products as well as oligomers which were absent in the Py-GC/MS of neat HTPB. This clearly shows that interaction between HTPB and AP occurs during the Py-GC/MS mode of analysis. Since it was clear from the DPMS study that AP does not influence HTPB primary degradation, the differences observed in the Py-GC/MS pyrograms are attributed to the interaction of AP with the primary degradation products of HTPB forming some new products in addition to the products coming from the neat HTPB. Further, AP induces formation of more aromatic compounds.

Table 3. Thermochemical Calculations[a]

$$\text{-(-CH}_2\text{-CH=CH-CH}_2\text{-)}_3\text{-}\ (\Delta H_f^o = +5.86) \longrightarrow 3\ \text{CH}_2\text{=CH-CH=CH}_2\ (\Delta H_f^o = +26.36) + \Delta H_d^o\ (+61.5) \quad (1)$$



(2)

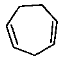
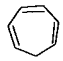
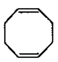
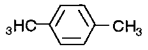
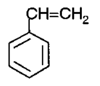
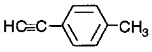
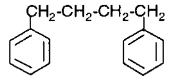
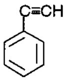
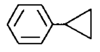
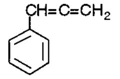
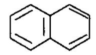
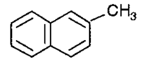
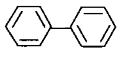
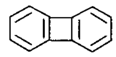
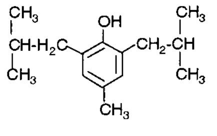
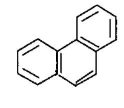


(3)

[a] ΔH_f values in were taken from refs 16 and 27. All the enthalpy values are in kcal/mol.

Table 4. Flash Pyrolysis-GCMS Products of Neat HTPB and HTPB/AP 80/20 wt %) at 700 °C

Peaks 1 to18 : neat HTPB.
Peaks 1 to 14, & 19 to 31 : HTPB/AP(80/20 wt%)

Peak no.	compounds	m/z
1.	$CH_2=CH-CH=CH_2$	54
2		68
3.		78
4.		94
5.		92
6.		108
7.		108
8.		106
9.		106
10.	$\text{-[CH}_2\text{-CH=CH-CH}_2\text{-]}_2\text{CH}_2\text{-CH=CH-}$	148
11.	$\text{-[CH}_2\text{-CH=CH-CH}_2\text{-]}_3\text{-}$	162
12.	Unidentified	162
13.	Unidentified	162
14.	Unidentified	198
15.		104
16.		116
17.		210
18.	unidentified	236
19.		80
20.		82
21.		102
22.	unidentified	118
23.		118
24.		116
25.	Unidentified	148
26.		128
27.		142
28.		154
29.		152
30.		220
31.		178

continued

Conclusions

Thermal degradation of HTPB appears to be more intriguing than it was thought in earlier reports. Primary chain scission leading to the formation of cyclics seems to be the most favored step. Hence, understanding the formation of 1,3-butadiene monomer in HTPB degradation is of foremost consideration. Under DPMS conditions, the formed primary fragments have very low residence time for undergoing secondary reactions as they are evolved very close to the ion source and

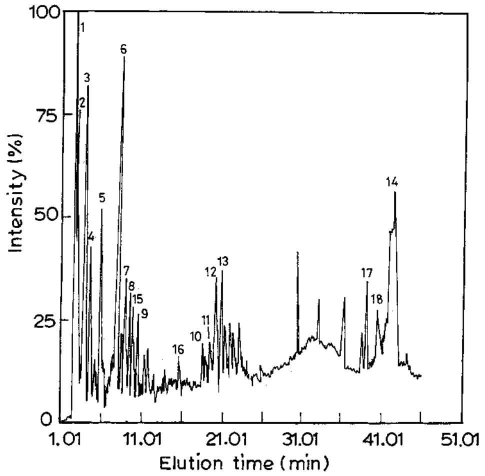


Figure 4. Gas chromatograms of the flash pyrolysates (Curie temperature, 700 °C) of heat HTPB.

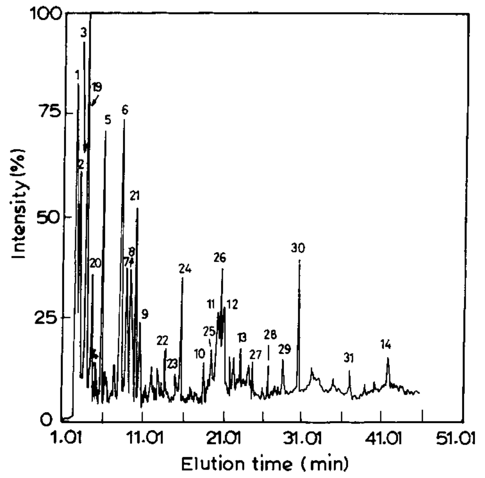


Figure 5. Gas chromatograms of the flash pyrolysates (Curie temperature, 700 °C) of HTPB/AP (80/20) mixture.

detected immediately. However, highly strained larger cyclics as well as some linear oligomers may decompose even under these conditions, forming 1,3-butadiene. Although the present study has shown, from the ΔH_f° data, that the major formation of 1,3-butadiene monomer comes from the dissociation of high molecular weight fragments and not through unzipping as has been proposed in the earlier reports, some fraction of monomer formation through other mechanisms cannot be completely ruled out. During the Py-GC/MS analysis, the primary products have sufficient residence time to undergo secondary reactions, and it is likely that even moderately stable cyclics may dissociate. Indeed, this is supported by the fact that the 1,3-butadiene concentration is much higher in Py-GC/MS mode compared to DPMS.

It has been observed that HTPB and HTPB/AP degradation products are almost identical in DPMS, but under Py-GC/MS conditions HTPB/AP degradation products are significantly different than neat HTPB. This would mean that AP or AP decomposition products interact with HTPB degradation products after the primary cleavage of HTPB chain. These oxidation reactions require sufficient time for interaction, and that is why they are observed under Py-GC/MS conditions and not in DPMS.

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