

Estimation of major volatile products from the first stage of the thermal decomposition of hydroxy-terminated polybutadiene binder

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Abstract

The major volatile products from the first stage of the thermal decomposition of hydroxy-terminated polybutadiene (HTPB), a composite solid propellant binder, were investigated quantitatively by means of discontinuous simultaneous techniques of thermal analysis and gas chromatography (TA–GC). The variation in the amounts of these products under various temperatures of thermal decomposition and at various heating rates was compared. The experimental results show that the hydroxy group in HTPB does not have a distinct effect on its thermal decomposition; consequently, the mechanism of thermal decomposition of HTPB is similar to that of polybutadiene.

INTRODUCTION

Recently, thermal analysis and gas chromatography (TA–GC) techniques have been widely applied to the analysis of the gases evolved from polymer thermolysis [1–5]. However, the major volatile products of the thermal decomposition of hydroxy-terminated polybutadiene (HTPB) binder have not yet been investigated quantitatively by these techniques. In modern solid rocket propellant, the HTPB binder plays an important role: it not only maintains the integrated structure of the solid propellant, but is also the indispensable fuel for stable combustion. Although a series of complex physicochemical changes in the burning process of modern solid rocket propellant has been treated mathematically by means of various approximate models, the results are always imperfect. In order to establish a more rational and more perfect model of the burning of the solid propellant, the energetics, kinetics, and products and mechanism of the thermal decomposition of the propellant material, especially the binder, must be known more precisely.

The thermal analysis of HTPB is an important method of characterizing it. Cohen et al. [6] have systematically investigated the role of various

binders (including HTPB) in solid propellant combustion. They have also identified the gases evolved from HTPB during thermal decomposition using mass spectrometry (MS), and have obtained mass numbers of 17 volatile products. We have studied the thermal decomposition of HTPB binder by means of TA-GC-MS [7], concluding that the decomposition of HTPB is indicated by two major stages of weight loss of different nature and indistinct separation, and evaluating the kinetic parameters of the decomposition process and the kinetic data with reference to solid propellant combustion. In addition, 20 gaseous products with less than 10 carbon atoms were obtained; their mass numbers were measured by MS [8]. On the basis of the above-mentioned studies, the present work investigates quantitatively a few of the major gaseous products evolved in the first stage of HTPB thermal decomposition and compares the effect of temperature and heating rate of the thermal decomposition on the amounts of those gases produced.

EXPERIMENTAL

A Thermoflex thermal analyser (TG-DTA-DTG simultaneous system) was interfaced with a 103 gas chromatograph (Analytic Instrument Factory, Shanghai, People's Republic of China). The interface, i.e. a multiplex automatic gas sampler constructed of 12-position microvolume valves placed in the thermostat, allowed up to 11 samples of the volatile products to be collected from each thermal analytical experiment.

The sample used in the present study was a commercially available HTPB resin (Chemical Plant, Fushun, People's Republic of China). The molecular weight of this resin is 4600, and the hydroxy content is 0.48 meq g^{-1} ; the *cis*-1,4 structure constitutes 14%, the *trans*-1,4 structure 62% and the 1,2-vinyl structure 21% of the total isomers. The GC column reagents were 60-80 mesh 102 white acid-washed support and silicone oil II (Reagent Factory, Shanghai, People's Republic of China).

All the experiments for thermal decomposition and testing were performed using combined TG-DTA-DTG techniques. The sample size was generally 15-20 mg; the weight of the reference compound, $\alpha\text{-Al}_2\text{O}_3$, was 18.0 mg. The ranges of the TG and DTA were 20 mg and $\pm 100 \mu\text{V}$, respectively. The DTG sensitivity was 0.5 mg min^{-1} . The flow rate of the atmosphere (high purity nitrogen) was 40 ml min^{-1} . Heating rates were 5, 10, 20, 30 and $40^\circ\text{C min}^{-1}$. The automatic gas sampler interface was maintained at 200°C to prevent condensation in the loops. A 10% Apiezon-L grease on 60-80 mesh 102 white support was packed in the upper part of the protected tube in the thermal analyser to prevent high boiling products with 10 carbons from entering the GC column. Before beginning heating, the specimen chamber and the gas line system of the thermal analyser were evacuated and high purity nitrogen was slowly injected. Then the pressure was equalized once again to remove completely any residual air. The volatile

products of the thermal decomposition were carried over by the high purity nitrogen. They were collected at 260, 280, 300, 320, 340, 350, 360, 370, 380 and 390 °C by the automatic gas sampler; then GC analysis was carried out.

The GC columns were 2 m × 3 mm stainless steel tubing packed with 7.8% silicone oil II on 60–80 mesh 102 white acid-washed support. The conditions of chromatographic analysis were as follows: the flow rate of the carrier gas (high purity nitrogen) was 20 ml min⁻¹, that of air 300 ml min⁻¹ and that of hydrogen 60 ml min⁻¹; the temperatures of injector and FID were 125 °C and 145 °C respectively; the GC columns were held at 40 °C for 4 min before being program-heated at 3 °C min⁻¹ to 120 °C and were then held isothermally at this temperature.

The experiments have shown that the volatile products from the first stage of thermal decomposition of HTPB are olefins alone [8] with approximately identical quantitative correction factors [9]. For this reason, the chromatographic peak area can be used to determine these volatile products.

RESULTS AND DISCUSSION

Figure 1 illustrates typical TG–DTA–DTG thermograms of HTPB obtained at a heating rate of 15 °C min⁻¹. It can be seen that below 300 °C there is almost no weight loss; an exothermic peak appears at about 165 °C and above 260 °C there are two major states of weight loss of indistinct separation, the first at 260–390 °C and the second above 390 °C.

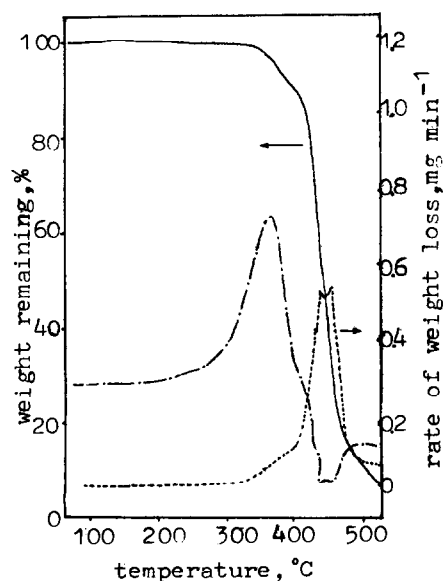


Fig. 1. TG (—), DTG (-----) and DTA (-·-·-) curves of HTPB: heating rate, 15 °C min⁻¹ in N₂ atmosphere (flow rate, 40 ml min⁻¹).

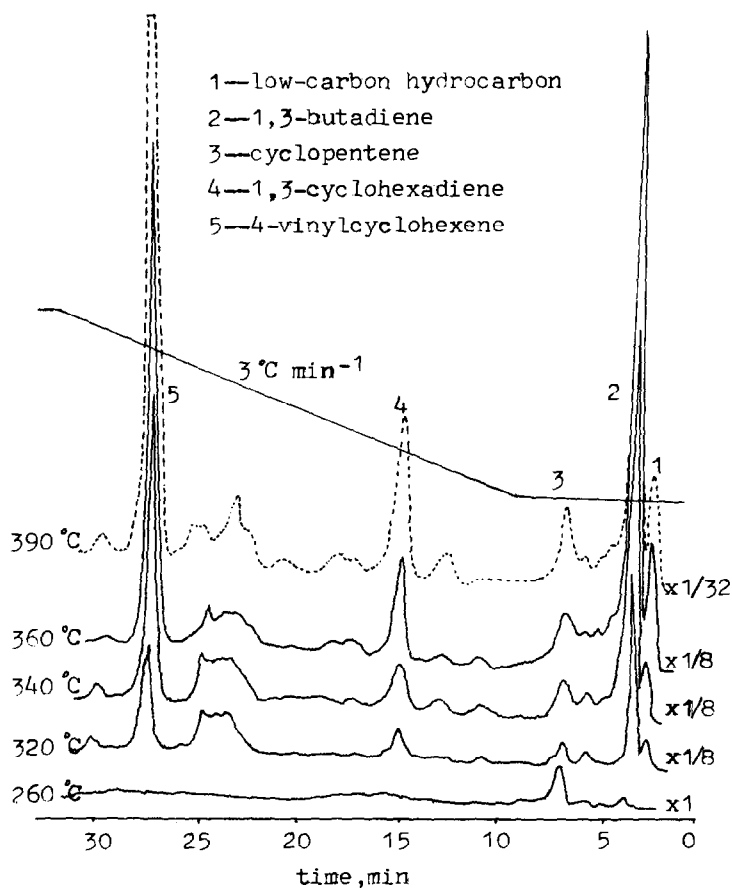


Fig. 2. Chromatograms of the thermal decomposition products of HTPB at different temperatures: heating rate, $20^{\circ}\text{C min}^{-1}$.

Chromatograms of volatile products from an HTPB sample at $20^{\circ}\text{C min}^{-1}$ heating rate and at different temperatures are shown in Fig. 2 in which a few major chromatographic peaks are low-carbon hydrocarbons

TABLE 1

Relative quantities of major volatile products at different temperatures produced from the thermal decomposition of HTPB binder.

Temp. ($^{\circ}\text{C}$)	Relative quantities (%)				
	Low-carbon hydrocarbons	Butadiene	Cyclopentene	1,3-Cyclohexadiene	4-Vinylcyclohexene
280	2.4	5.7	3.0	3.8	11.6
320	4.7	17.4	4.7	5.4	16.6
350	5.2	29.8	3.7	6.4	21.8
380	7.6	35.8	4.8	6.7	23.1

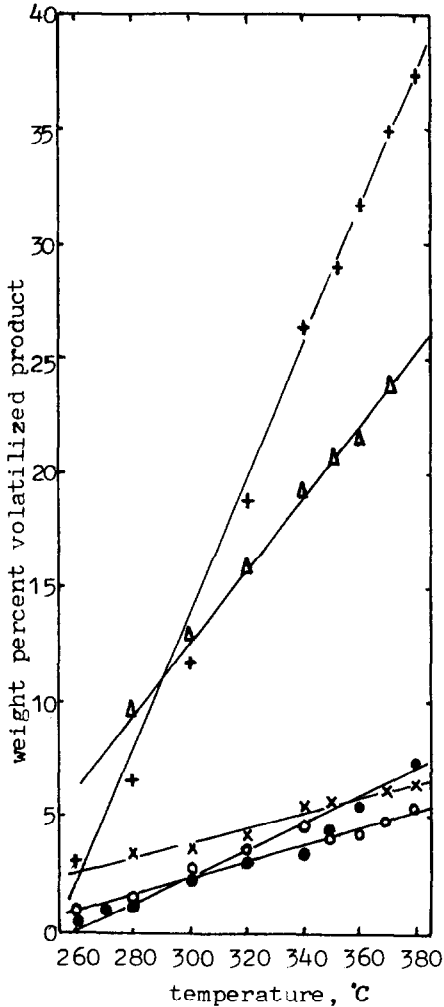


Fig. 3. Amounts of main products vs. temperature (heating rate in parentheses): +, 1,3-butadiene, ($20^{\circ}\text{C min}^{-1}$); Δ , 4-vinylcyclohexene ($5^{\circ}\text{C min}^{-1}$); \times , 1,3-cyclohexadiene, ($40^{\circ}\text{C min}^{-1}$); \circ , cyclopentene ($30^{\circ}\text{C min}^{-1}$); \bullet , low-carbon hydrocarbons ($40^{\circ}\text{C min}^{-1}$).

(ethylene etc.), 1,3-butadiene, cyclopentene, cyclohexadiene and 4-vinylcyclohexene, respectively [7,8]. During the initial post-thermal decomposition there are only small amounts of butadiene and cyclopentene. With increasing temperature, other gases are produced in succession. Their amounts also increase with temperature, and the increases in the amounts of 1,3-butadiene and 4-vinylcyclohexene are the greatest (Table 1).

Figure 3 shows the relationship between the relative amounts of low-carbon hydrocarbons (cyclopentene etc.) and temperature. Table 1 lists the relative quantities of major volatile products at different temperatures in the thermal decomposition of HTPB binder (the calculation was based on the

total amount of all the evolved gaseous products, i.e. the total of all the chromatographic peak areas was taken as 100%). The data in Table 1 show clearly that at the approximate end of the first stage of HTPB thermal decomposition (380°C), the major volatile products account for about 80% of the total amount of all evolved gases.

It has been determined experimentally that the heating rate has a strong effect on the change in the relative amounts of the gaseous products with temperature. In general, except for butadiene, the relative amounts of the gases produced with increasing temperature increases much more rapidly at low rates of heating than at high rates of heating ($40^{\circ}\text{C min}^{-1}$); however, the behaviour of butadiene is exceptional (Fig. 4).

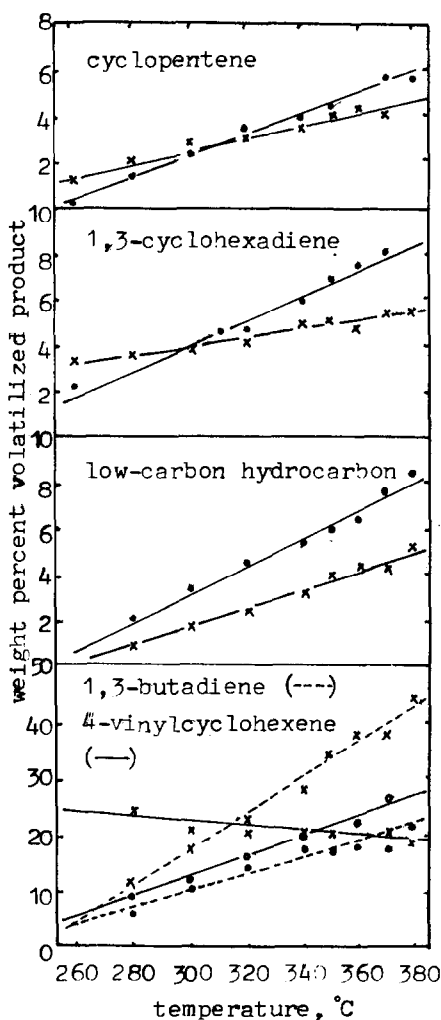


Fig. 4. Effect of heating rate on relation between amounts of main products and temperature: ●, $5^{\circ}\text{C min}^{-1}$; ×, $40^{\circ}\text{C min}^{-1}$.

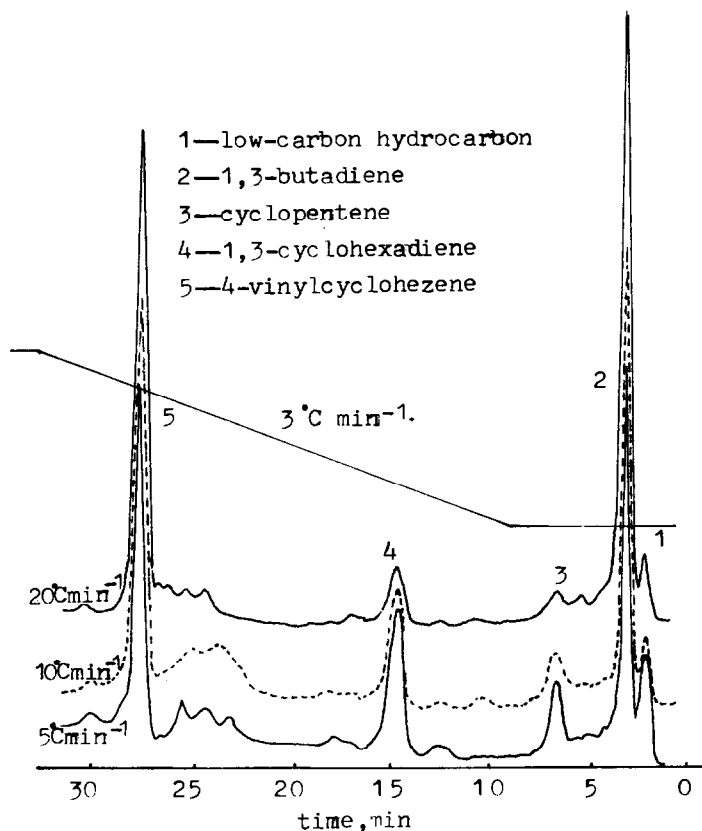


Fig. 5. Chromatograms of the thermal decomposition products of HTPB at 350°C with different heating rates.

Figure 5 shows a group of chromatograms at 350°C at different heating rates; although the temperature of the thermal decomposition is identical, the quantities of the main volatile products vary greatly because of the different heating rates. The detailed results of the experiments show the following general relationships: with increasing heating rate, the amounts of low-carbon hydrocarbons and cyclohexadiene decrease, and that of 4-vinylcyclohexene increases slowly, but the amounts of butadiene and cyclopentene appear to follow a different trend: in the initial region of the thermal decomposition (260–320°C) the amount of butadiene decreases and that of cyclopentene increases; however, in the main temperature region of the thermal decomposition (320–390°C) the reverse occurs (Fig. 6).

Tamura and Gillham [10] have reported the effect of heating rate on the four main degradation products formed during 15% weight loss of 1,4-polybutadienes. In their study, the amounts of 1,3-butadiene and 4-vinylcyclohexene increased linearly and that of cyclopentene decreased linearly; however, production of 1,3-cyclohexadiene appeared to be unaffected by heating rate. In addition, the sum of the amounts of 4-vinylcyclohexene and

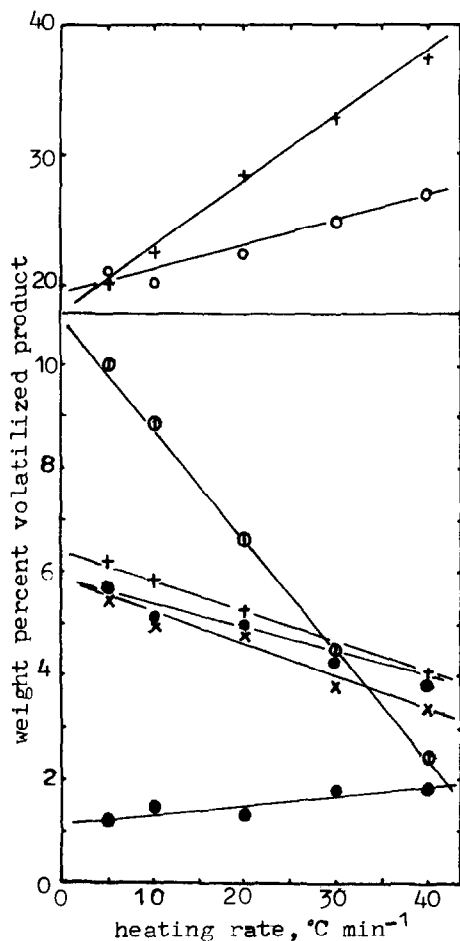


Fig. 6. Effect of heating rate on amounts of main products at different temperatures: +, 1,3-butadiene (upper, at 350°C; lower, at 280°C); o, 4-vinylcyclohexene at 350°C; o, 1,3-cyclohexadiene at 370°C; x, low-carbon hydrocarbons at 350°C; ●, cyclopentene (upper, at 370°C; lower, at 280°C).

cyclopentene appeared to be constant (Fig. 7). Our experimental results (Fig. 8) show that except in the initial stages of thermal decomposition, the variation with heating rate in the amounts of the four major products formed in the first stage of HTPB thermal decomposition is similar to that found for 1,3-polybutadiene; only the amount of 1,3-cyclohexadiene decreased slightly with increasing heating rate. The sum of the amounts of 4-vinylcyclohexene, cyclopentene and 1,3-cyclohexadiene is also roughly constant, and remarkably similar to the above results for 1,3-polybutadiene. Thus, it seems that the mechanism of the thermal decomposition of HTPB in the first stage is similar to that of 1,4-polybutadiene. In fact, HTPB and 1,4-polybutadiene have the same structure, the only difference being the terminating group. Using another method, we have proved that there is no

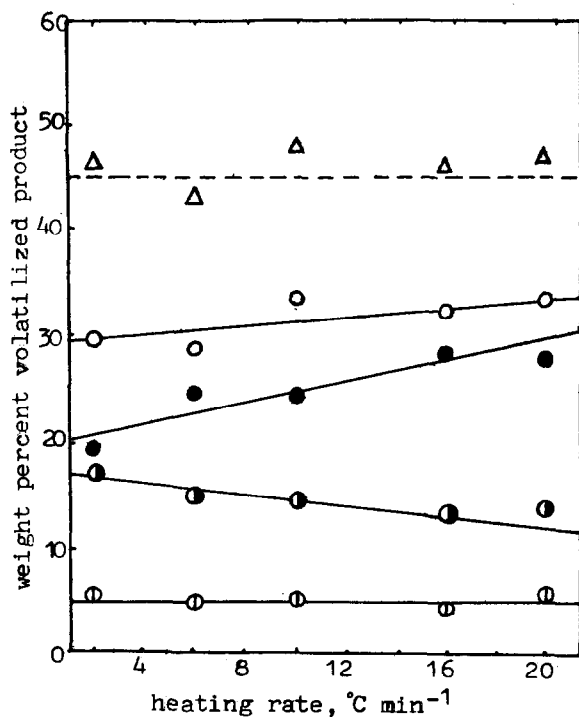


Fig. 7. Effect of heating rate on amounts of main products formed during 15% weight loss of 1,3-polybutadiene: ●, 1,3-butadiene; ○, cyclopentene; ○, 1,3-cyclohexadiene; ○, 4-vinylcyclohexene; Δ, cyclopentene + 4-vinylcyclohexene. (From ref. 10).

clear relation between the hydroxy-terminating group of HTPB and the thermal decomposition behaviour of HTPB. Thus, it can be considered to be reasonable that the hydroxy-terminated HTPB has no effect on its thermal

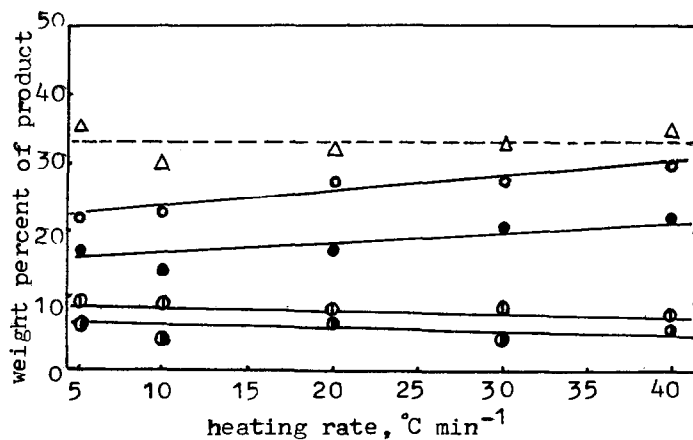


Fig. 8. Effect of heating rate on amounts of main thermal decomposition products of HTPB at 390 °C: ○, 1,3-butadiene; ●, 4-vinylcyclohexene; ○, 1,3-cyclohexadiene; ●, cyclopentene; Δ, 4-vinylcyclohexene + 1,3-cyclohexadiene + cyclopentene.

decomposition. This is because the hydroxy-terminating group in HTPB is difficult to ionize as it is nearly neutral; in addition, it is present in HTPB at a very low level (usually 2% for HTPB produced by free-radical polymerization; in the present study, 2.2%), so that its effect on the thermal decomposition of HTPB is negligible.

CONCLUSIONS

In the first stage of the thermal decomposition of HTPB, the major volatile products are 1,3-butadiene, 4-vinylcyclohexene, cyclopentene, 1,3-cyclohexadiene and low-carbon hydrocarbons such as ethylene etc. Increasing the temperature of the thermal decomposition, increases the gases produced in varying degrees, with 1,3-butadiene and 4-vinylcyclohexene increasing at a much faster rate. At the end of the first stage, their total volume is approximately 80% of all the gases evolved.

With increasing heating rate, the butadiene (monomer) content of the thermal decomposition fractions increases rapidly with increasing temperature, while the other products decrease or only increase slowly.

In the main thermal decomposition region of the first stage of weight loss (320–390 °C), except for 1,3-butadiene monomer (depolymerization product) which increases rapidly with increasing heating rate, the most cyclized and pyrolyzed products all decrease in quantity; this shows that increasing the heating rate favours depolymerization while cyclization and pyrolysis are not favoured.

The process and mechanism of the thermal decomposition of HTPB are similar to that of 1,4-butadiene polymer and the hydroxy-terminating group has no distinct effect on the decomposition.

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