

# Thermogravimetric and Mass-Spectrometric Study of the Thermal Decomposition of PBCT Resins

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## Synopsis

The thermal decomposition of three commercial samples of carboxy-terminated polybutadiene (PBCT) resins was studied by thermogravimetric analysis (TGA) at heating rates varying from 2° to 100°C/min. Kinetic parameters of the decomposition process at different heating rates were evaluated by means of the Fuoss method.<sup>1</sup> The decomposition process and the activation energy values are found to be dependent on heating rate. Mass-spectrometric analysis of the decomposition products shows that the pyrolysis products of PBCT resins are mainly low molecular weight hydrocarbons: ethylene, acetylene, butadiene, propadiene, vinylcyclohexene, etc. The rates of evolution of these hydrocarbon products vary with the carboxy content of the PBCT resin. Based on this, a carbonium ion mechanism has been suggested for the thermal decomposition. The data generated from this work are of importance for a consideration of the mechanism of combustion of composite solid propellants based on PBCT binders.

## INTRODUCTION

Composite solid propellant is a conglomerate of an inorganic oxidizer embedded in a polymeric matrix. The binder must maintain the structural integrity of the grain as well as provide the combustible materials during the steady-state deflagration process.<sup>2,3</sup> The combustion of the propellant proceeds through a series of complex physicochemical processes.<sup>4-8</sup> Many attempts have been made to explain the phenomena on a rational basis. No mathematically tractable model could so far take all reaction sequences into consideration. The burning process may take place in varying degrees in the gas phase and on the propellant surface. Condensed-phase reactions may also play an important role.<sup>9</sup> Decomposition of the oxidizer and the binder is effected by heat feedback from the combustion zone. Analytical modeling, therefore, requires detailed information on the kinetics and mechanism of thermal decomposition of the propellant materials. Considerable work<sup>10</sup> has already been carried out on the thermal decomposition of ammonium perchlorate (AP), the commonly used oxidizer in modern rocket technology. However, only few attempts have been made to study the kinetics and mechanism of the thermal decomposition of common propellant binders.<sup>11-16</sup>

Polybutadiene binders play an important role in modern rocket propellant manufacture. Functionally terminated liquid polybutadiene polymers are available in different molecular weight ranges. The propellant-grade materials

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are mainly carboxy-terminated polybutadiene (PBCT), hydroxy-terminated polybutadiene (PBHT), and the polybutadiene-acrylic acid-acrylonitrile copolymer (PBAN). These liquid polymers are synthesized by a variety of techniques<sup>17</sup>: free radical, ionic, oxidative degradation, etc. The microstructure of the polymer (cis, trans, vinyl ratio) varies according to the method of manufacture. Even though there have been many studies in recent times<sup>18-22</sup> on the thermal decomposition of polybutadiene polymers, their functionally terminated low molecular weight analogs have not yet been investigated on a systematic basis.<sup>23</sup> This work is an attempt to evaluate the kinetic parameters for the thermal decomposition of PBCT binders and to analyze their pyrolysis products by means of a mass spectrometer.

### EXPERIMENTAL

Three commercially available PBCT resins have been used in the present study. Table I presents the details of these resins. Molecular weights of the resins have been determined by measuring the dilute solution viscosity using toluene as the solvent and applying the equation<sup>17</sup>

$$[\eta] = 6.75 \times 10^{-4} M^{0.645}$$

Microstructure values were taken from reference 3. Thermogravimetric experiments were carried out in a du Pont 990 thermal analyzer. A platinum boat serves as sample container. The thermocouple is made of Chromal-Alumel and is placed near the sample boat. The instrument permits heating rates from 0.5° to 100°C/min. in steps. The experiments were conducted in atmospheres of air and nitrogen, by purging the required gas at a rate of about 50 ml/min.

The mass-spectrometric analysis of the decomposition products was carried out in an Associated Electric Industries MS 10 mass spectrometer. About 500 mg of the resin is taken in a 90° bent glass tube and connected to the "ion source cage" of the mass spectrometer through a molecular leak. The sample tube is then evacuated to a pressure of about 10<sup>-8</sup> to 10<sup>-9</sup> torr and the background intensities of the gases present in the system are noted. The sample tube is then surrounded by a tubular furnace maintained at 500°C. The decomposition products are then led into the ion source cage until such time that an optimum pressure increase is noticed (about 1 hr). At the end of the experiment, the

TABLE I  
Analytical Results of PBCT Resins

|                          | HC 434                         | Hycar<br>PBCT                 | Butarez<br>CTL                |
|--------------------------|--------------------------------|-------------------------------|-------------------------------|
| Manufacturer             | Thiokol Chemical Corp., U.S.A. | Goodrich Chemical Co., U.S.A. | Philips Petroleum Co., U.S.A. |
| Polymerization technique | free radical                   | free radical                  | ionic                         |
| Molecular weight         | 5346                           | 6471                          | 6124                          |
| Carboxy content, meq/g   | 0.0525                         | 0.0382                        | 0.0239                        |
| Iodine value             | 428.5                          | 467.4                         | 436.8                         |
| Microstructure           |                                |                               |                               |
| vinyl, %                 | 20.4                           | 19.8                          | 27                            |
| trans                    | 51.5                           | 50.9                          | 39                            |
| cis                      | 28.1                           | 29.3                          | 34.0                          |

furnace is removed and the sample tube is cut off from the mass spectrometer by means of a stopcock. The relative intensities of the decomposition product gases and their fragmentation products are then recorded. The difference between this reading and the background reading gives the relative intensity corresponding to the fragment.

## RESULTS

Figures 1, 2, and 3 show the thermogravimetric (TG) and differential thermogravimetric (DTG) traces for HC 434, Hycar PBCT, and Butarez CTL resins in a stream of nitrogen gas at heating rates of 2°, 10°, 20°, 50°, and 100°C/min. Table II presents the temperature of inception ( $T_i$ ), maximum rate ( $T_m$ ), and completion ( $T_f$ ) of decomposition. Figure 4 shows the TG traces of Butarez CTL in atmospheres of nitrogen and air at a heating rate of 10°C/min.

Table III presents values of the kinetic parameters for the thermal decomposition of the binders calculated by the Fuoss method<sup>1</sup> using the equations

$$E_a = -(RT_i^2/W_i)(dW/dT)_i \quad (1)$$

where  $E_a$  is the activation energy for the decomposition;  $T_i$  and  $W_i$  are the temperatures and weight at the point on the TG curve where it goes from concave-down to convex-up; and  $dW/dT$  is the corresponding inflection slope. Having determined  $E_a$  from eq. (1), the preexponential factor ( $A$ ) was computed from the equation

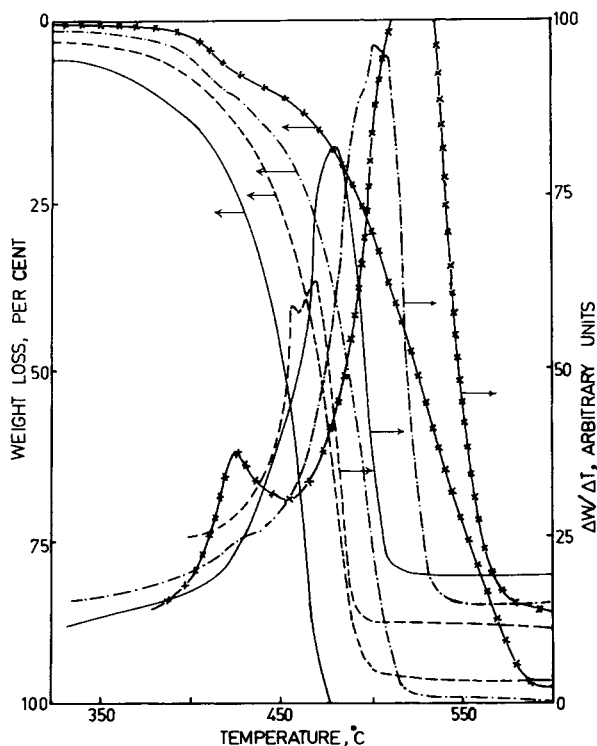


Fig. 1. TG/DTG traces of HC 434 at heating rates of 5°C/min (—), 10°C/min (-----), 20°C/min (-----), and 50°C/min (—x—x—). Sample weight, 5 mg; atmosphere, N<sub>2</sub>.

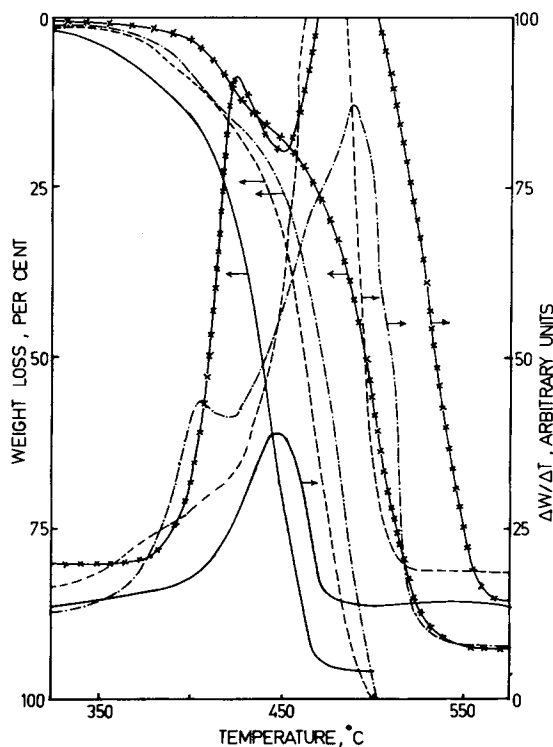


Fig. 2. TG/DTG traces of Hycar PBCT at heating rates of 2°C/min (—), 10°C/min (-----), 20°C/min (-·-·-·-·-), and 50°C/min (—x—x—x—x—x—). Sample weight, 5 mg; atmosphere, N<sub>2</sub>.

TABLE II  
Decomposition Temperatures of PBCT Resins

| Resin type  | Heating rate, °C/min | Temperature of inception $T_i$ , °C | Temperature of maximum rate $T_m$ , °C | Temperature of completion $T_f$ , °C |
|-------------|----------------------|-------------------------------------|--|--------------------------------------|
| HC 434      | 2                    | 300                                 | 450                                    | 480                                  |
|             | 5                    | 300                                 | 465                                    | 475                                  |
|             | 10                   | 325                                 | 480                                    | 500                                  |
|             | 20                   | 350                                 | 500                                    | 535                                  |
|             | 50                   | 375                                 | 525                                    | 535                                  |
|             | 100                  | 390                                 | 530                                    | 540                                  |
| Hycar PBCT  | 10                   | 350                                 | 475                                    | 500                                  |
|             | 20                   | 375                                 | 485                                    | 505                                  |
|             | 50                   | 385                                 | 500                                    | 530                                  |
| Butarez CTL | 10                   | 325                                 | 465                                    | 500                                  |
|             | 50                   | 350                                 | 492                                    | 520                                  |
|             | 100                  | 400                                 | 525                                    | 555                                  |

$$A = -(RH/W_i)(dW/dT)_i e^{E_a/RT_i} \quad (2)$$

where  $RH$  is the heating rate. In the case of an  $n$ th order reaction, eq. (1) takes the following form:

$$E = -(nRT_i^2/W_i)(dW/dT)_i \quad (3)$$

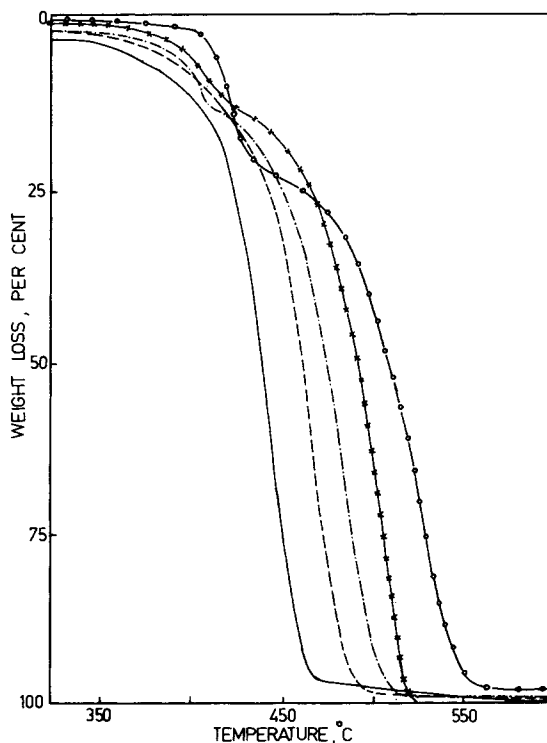


Fig. 3. TG traces of Butarez CTL at heating rates of 2°C/min (—), 10°C/min (-----), 20°C/min (-----), 50°C/min (—×—×—×—), and 100°C/min (—○—○—○—). Sample weight, 5 mg; atmosphere, N<sub>2</sub>.

TABLE III  
Kinetic Parameters<sup>a</sup> for Thermal Decomposition of PBCT Resins

| Resin type          | Heating rate, °C/min | Preexponential factor log A | Activation energy E <sub>a</sub> , kcal/mole |
|---------------------|----------------------|-----------------------------|--|
| HC 434              | 20                   | 9.05                        | 38.5   |
|                     | 50                   | 6.09                        | 30.2   |
| Hycar PBCT          | 10                   | 8.34                        | 36.3   |
|                     | 50                   | 5.92                        | 27.2   |
| Butarez CTL         | 10                   | 8.4                         | 36.1   |
|                     | 50                   | 6.6                         | 29.3   |
|                     | 100                  | 5.3                         | 24.5   |
| CTPB <sup>b</sup>   | —                    | A = 3.4 × 10 <sup>5</sup>   | 28   |
| HC 434 <sup>c</sup> | —                    | A = 12.8                    | 10.5   |

<sup>a</sup> Values calculated by the Fuoss method<sup>1</sup>; E<sub>a</sub> calculated by the Freeman-Carroll method<sup>24</sup> gives a value of 32 kcal/mole for Hycar PBCT at a heating rate of 10°C/min.

<sup>b</sup> Values from ref. 12.

<sup>c</sup> Values from ref. 27.

The activation energy for the decomposition of PBCT resins was calculated assuming a value of 1 for the order of reaction as shown by earlier workers.<sup>12</sup> As a test for this method of calculation, activation energies and order of reactions were calculated in a few typical cases by the Freeman-Corrol method.<sup>24,25</sup> Values calculated from both these methods are quite comparable.

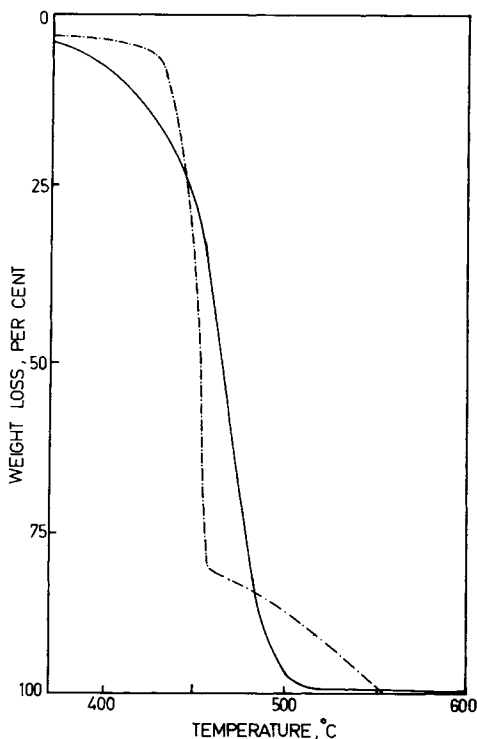


Fig. 4. TG traces of Butarez CTL in N<sub>2</sub> (—) and air (-----) at a heating rate of 10°C/min. Sample weight, 5 mg.

Table IV presents the mass spectra of the decomposition products from all the three PBCT resins at 500°C. The product species from all the three resins are almost the same and the relative intensities are also comparable, irrespective of their methods of preparation and microstructure. Butarez CTL, for example, is prepared by lithium-initiated anionic polymerization, whereas the Hycar PBCT and HC 434 resins are prepared by free-radical polymerization. In free-radical polymerization, the initiator differs in both cases. Even though the manufacturers do not disclose the exact initiator used in the polymerization, Hycar PBCT seems to have been prepared using azobisisocyanovaleric acid initiator since the IR spectrum of this resin shows a strong band at 2200 cm<sup>-1</sup>, corresponding to the —CN group.

The PBCT resins selected in this investigation differ mainly in their carboxy content and microstructure. From Table IV, on the mass spectra of the decomposition products, the concentrations of these products are found to correlate to the carboxy contents.

## DISCUSSION

The PBCT resins are mainly used in the manufacture of composite propellants. In the propellant application, these resins are mixed with the oxidizer and other additives, including the curing agents. The curing agents used in this case are a diepoxide and a trifunctional aziridine derivative (MAPO). The curing re-

TABLE IV  
Mass Spectra of the Pyrolysis Products of CTPB Resins

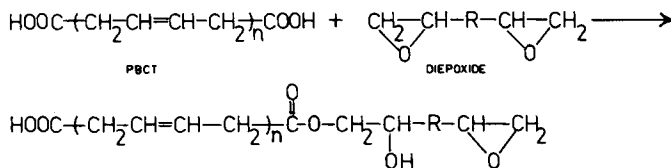
| <i>m/e</i> | Probable assignment<br>of fragment  | Relative ion intensities |            |             |
|------------|---|--------------------------|------------|-------------|
|            |   | HC 434                   | Hycar PBCT | Butarez CTL |
| 12         | C <sup>+</sup>  | 3.85                     | 1.8        | 2.0         |
| 13         | CH <sup>+</sup>   | 3.4                      | 2.1        | 1.0         |
| 14         | CH <sub>2</sub> <sup>+</sup>  | 8.4                      | 4.2        | 1.75        |
| 15         | CH <sub>3</sub> <sup>+</sup>  | 14.8                     | 12.0       | 6.8         |
| 16         | CH <sub>4</sub> <sup>+</sup> (methane), O <sup>+</sup>                      | 16.7                     | 12.8       | 7.8         |
| 17         | OH <sup>+</sup>   | 2.2                      | 0.8        | 0.5         |
| 18         | H <sub>2</sub> O <sup>+</sup>   | 5.0                      | 2.5        | 2.0         |
| 25         | C <sub>2</sub> H <sup>+</sup>   | 8.0                      | 3.8        | 2.4         |
| 26         | C <sub>2</sub> H <sup>+</sup> (acetylene)                                   | 4.2                      | 2.1        | 13.0        |
| 27         | C <sub>2</sub> H <sub>3</sub> <sup>+</sup>                                  | 81.7                     | 4.0        | 25.0        |
| 28         | C <sub>2</sub> H <sub>3</sub> <sup>+</sup> (ethylene), CO <sup>+</sup>      | 125                      | 41         | 33.0        |
| 29         | C <sub>2</sub> H <sub>5</sub> <sup>+</sup>                                  | 14.6                     | 8.3        | 6.0         |
| 30         | CH <sub>2</sub> O <sup>+</sup> , C <sub>2</sub> H <sub>6</sub> <sup>+</sup> | 3.0                      | 2.1        | 1.4         |
| 32         | O <sub>2</sub> <sup>+</sup>   | 4.0                      | 0.6        | 1.0         |
| 37         | C <sub>3</sub> H <sup>+</sup>   | 6.0                      | 2.4        | 1.8         |
| 38         | C <sub>3</sub> H <sub>2</sub> <sup>+</sup>                                  | 8.5                      | 3.6        | 2.8         |
| 39         | C <sub>3</sub> H <sub>3</sub> <sup>+</sup>                                  | 80.0                     | 34.0       | 28.0        |
| 40         | C <sub>3</sub> H <sub>4</sub> <sup>+</sup> (propadiene)                     | 10.0                     | 3.7        | 3.4         |
| 41         | C <sub>3</sub> H <sub>5</sub> <sup>+</sup>                                  | 34.0                     | 12.9       | 14.0        |
| 42         | C <sub>3</sub> H <sub>6</sub> <sup>+</sup>                                  | 8.0                      | 4.5        | 5.0         |
| 43         | C <sub>3</sub> H <sub>7</sub> <sup>+</sup>                                  | 3.3                      | 2.3        | 2.8         |
| 44         | C <sub>3</sub> H <sub>8</sub> <sup>+</sup> , CO <sub>2</sub> <sup>+</sup>   | 2.3                      | 1.4        | 1.4         |
| 50         | C <sub>4</sub> H <sub>2</sub> <sup>+</sup>                                  | 12.0                     | 4.8        | 4.0         |
| 51         | C <sub>4</sub> H <sub>3</sub> <sup>+</sup>                                  | 11.0                     | 4.4        | 3.8         |
| 52         | C <sub>4</sub> H <sub>4</sub> <sup>+</sup>                                  | 6.0                      | 2.4        | 2.0         |
| 53         | C <sub>4</sub> H <sub>5</sub> <sup>+</sup>                                  | 23.0                     | 8.5        | 8.2         |
| 54         | C <sub>4</sub> H <sub>6</sub> <sup>+</sup> (butadiene)                      | 35                       | 14.0       | 21.0        |
| 55         | C <sub>4</sub> H <sub>7</sub> <sup>+</sup>                                  | 6.0                      | 2.0        | 6.5         |
| 56         | C <sub>4</sub> H <sub>8</sub> <sup>+</sup> (butene)                         | 5.0                      | 2.0        | 6.2         |
| 66         | C <sub>5</sub> H <sub>6</sub> <sup>+</sup> (cyclopentadiene)                | 8.0                      | 2.0        | 1.6         |
| 78         | C <sub>6</sub> H <sub>6</sub> <sup>+</sup> (benzene)                        | 4.0                      | 1.2        | 1.0         |
| 108        | C <sub>8</sub> H <sub>12</sub> <sup>+</sup> (vinylcyclohexene)              | 0.2                      | 0.1        | 1.0         |

action, depicted in Figure 5, converts the propellant slurry into a solid mass. The desired mechanical properties are achieved by varying the ratio of the diepoxide and MAPO.

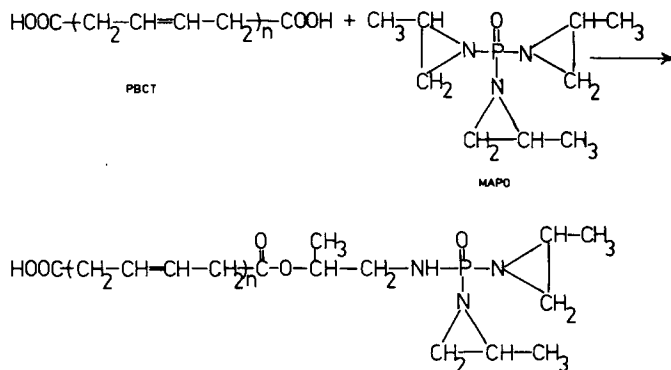
The curing reaction in a PBCT propellant introduces the ester and P—N linkages into the net work structure. The concentration of these links, which are relatively weaker than the main-chain carbon-carbon bonds, are very low and can be expected to cleave in the initial stages of the degradative process. Hence, the degradation reactions that provide the fuel elements for gas-phase reactions with the oxidizer decomposition reactions come from the pyrolysis of the polybutadiene chain. However, one difference exists between this study and the polybutadiene pyrolysis in the propellant system. In the propellant system, the carboxy endgroups are converted into ester linkages. In free PBCT resin, the free carboxy groups exist as such, and they are found to have mechanistic implications as explained later.

The important feature noted from the TGA traces is the effect of heating rate on the decomposition kinetics and mechanism. Among the three resins, HC 434

## a) Chain extension reaction



## b) Cross linking reaction



MAPO : TRIS(METHYL AZIRIDINYL) PHOSPHINE OXIDE

Fig. 5. Curing reactions of PBCT-based propellants.

is found to start decomposing at the lowest temperature at any particular heating rate. This resin having the highest carboxy content, it is found to produce larger amounts of hydrocarbon decomposition products compared to the other two resins. It can be inferred from these data that the carboxy group acts as an initiator in the decomposition of the polybutadiene backbone.

Recent investigation on the effect of heating rate on the thermal degradation of polybutadiene<sup>19</sup> has shown that the pyrolysis takes place in two stages at all heating rates. However, in the present study with PBCT resins, TGA traces at heating rates of 2°, 10°, and 20°C/min show one sigmoid curve and a single DTG peak only corresponding to a single-stage mechanism. On the other hand, when the heating rate is raised to 50°C/min, two distinct weight loss regions are observed, and the differential plot also shows two peaks. Brazier and Schwartz<sup>19</sup> have also observed an increase in the first-stage rate of decomposition as the heating rate is increased. The first stage in the thermal degradation of polybutadiene is ascribed to partial pyrolysis of the polymer followed by cyclization. The cyclized product decomposes in the second stage. The first-stage reaction is found to be catalyzed by the presence of oxygen, as seen in Figure 4. Two distinct weight loss regions are very much evident even at a heating rate of 10°C/min in the presence of air. The same resin under identical conditions decomposes in a single stage in the presence of nitrogen.

The kinetics of thermal decomposition show that the activation energy values are dependent on the heating rate. Such a heating rate dependence has recently

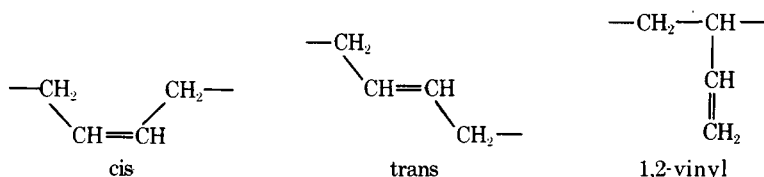


been reported in the thermal decomposition of various propellants also.<sup>26</sup> In the present study, the activation energy decreases with the heating rate in all cases. The values are almost the same at a particular heating rate, irrespective of the nature of the PBCT and its properties. The activation energy values evaluated in the present study are comparable with those calculated by Varney and Strahle<sup>12</sup> from DSC experiments. However, they differ very much from the values reported by Cohen et al.<sup>27</sup> calculated from arc image data.

The heating rate dependence of the kinetics of decomposition is significant from a consideration of the mechanism of combustion of propellants. Steady-state combustion models consider that the polymer pyrolyzes to gaseous species for the reaction with the oxidizer decomposition products. The aim of laboratory thermolysis experiments on binders has been to extrapolate the data obtained from such studies to combustion conditions. However, several important questions concerning the applicability of the results of these laboratory tests to propellant combustion conditions have never been adequately answered. Perhaps the most serious question relates to the validity of extrapolating data obtained at heating rates of less than 1°C/sec to combustion situations where the heating rate is estimated to be of the order of 10<sup>5</sup>°C/sec. It has also to be expected that considerable structural modification may take place in the polymer backbone at different heating rates. The importance of such a heating rate effect has not been experimentally established for propellant binders except the high heating rate studies of Bouck et al.<sup>16</sup> Our studies clearly establish that the kinetics of PBCT binder thermal decomposition is heating rate dependent, and hence caution must be exercised in extrapolating low heating rate decomposition data to calculate combustion parameters.

The surface temperature of AP-PBAN propellant has been estimated to be approximately 600–700°C regardless of pressure.<sup>28</sup> The experimental condition under which the mass-spectrometric experiments have been carried out to identify the decomposition products is 500°C, and this temperature is comparable to the propellant surface temperature. Hence, it is reasonable to expect that the decomposition products observed in this experiment are almost the same as those produced under combustion conditions.

PBCT resins produced by the anionic and free-radical technique are a mixture of the *cis*-, *trans*-, and 1,2-vinyl structures:



The concentrations of the three structures in the PBCT resins are given in Table I. In addition, the three resins differ in their carboxy content. It is seen from the mass spectra as given in Table IV that the concentrations of the various hydrocarbon species are in the order of the carboxy contents of the resins. The carboxy group can easily ionize to produce a proton, which in turn can initiate



combustion process. The decomposition products of ammonium perchlorate (AP) are oxygen and oxides of chlorine and nitrogen.<sup>10</sup> Since the binder produces simple molecular species such as ethylene, acetylene, butadiene, etc., the combustion chemistry of polybutadiene-AP-based propellants can be considered to be the reactions between these gaseous species. On the basis of such simplified models, laboratory investigations have been carried out with AP and low molecular weight hydrocarbons.<sup>33</sup>

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