ELSEVIER
Thermochimica Acta 285 (1996) 109–117
thermochimica acta

A study of the thermal decomposition of biguanidinium diperchlorate using thermogravimetry and mass spectroscopy

David Dollimore *, Anthony Martin, A. Alan Pinkerton

The Chemistry Department, The University of Toledo, Toledo, OH 43606, USA

Received 31 July 1995; accepted 28 January 1996

Abstract

The thermal decomposition of biguanidinium diperchlorate has been studied by thermogravimetry in a nitrogen atmosphere and by mass spectrometry. The kinetics of the decomposition have been found from these experiments to be very rapid and exothermic. A first order (F1) mechanism has been fitted to the decomposition up to the point of inflection.

Keywords: Biguanidinium perchlorate; Differential thermal analysis; Energetic reactions; Kinetic analysis; Thermogravimetric analysis

1. Introduction

It is known that most simple guanidinium salts decompose by a vigorous exothermic reaction [1]. A number of these salts have been examined using thermogravimetry. Biguanidinium diperchlorate was prepared as described in the experimental section. A mixture containing both biguanidinium perchlorate and biguanidinium di-perchlorate was reported as explosive [2]. A search of the literature failed to reveal any other relevant information concerning the thermal decomposition of biguanidinium salts. Upon heating in air, biguanidinium diperchlorate decomposed rapidly with larger amounts (more than 3 mg) exploding with a green flash. Those results are not included here, as the thermocouple registered the explosion as a spike in the heating rate. A detailed report on this light emission is the subject of a future publication. Guanidinium salts have also displayed light emission during decomposition [3].

---

* Corresponding author.

PII S0040-6031(96)02876-6

2. Experimental

2.1. Materials

Biguanidinium perchlorate has the formula $[C_2N_5H_9]^+[ClO_4]_2^-$. The biguanidinium diperchlorate was prepared by taking stoichiometric amounts of $[C_2N_5H_8]^{2+}$ $[SO_4]^{2-}$. H_2O and $Ba(ClO_4)_2 \cdot 3H_2O$. These two compounds were dissolved in water. The insoluble $BaSO_4$ was filtered off. The resultant solution was left to crystallize.

2.2. Equipment and procedures

The thermal analysis was carried out using a DuPont 1090 unit. The technique applied here was to use a small sample of biguanidinium diperchlorate (less than 3 mg) and a variety of heating rates (noted in the tables and figures). A platinum pan and an atmosphere of flowing nitrogen were used in all the TG runs. Temperature calibration was carried out using the fusible link method. The temperature could be read from the record to one decimal point but it is better to regard the temperature as correct to within one degree.

A stand-alone HP 5988 Mass Spectrometer was used with a direct insertion probe. The temperature at the probe started at 30°C and was increased at 5°C min^{-1} up to 350°C. Scans were made approximately every second.

3. Results and discussion

The small sample size (less than 3 mg) used in the TG experiments means that the final amount of material left is not well defined. A typical TG plot for biguanidinium diperchlorate is given in Fig. 1. On this figure is noted a start temperature representing the beginning of the main reaction, an inflection point representing the maximum in the peak temperature (DTG) and an end temperature at which the main peak in the DTG is overlapped by the next stage. In the kinetic analysis the stage up to the peak temperature is shown to correspond to the decelerating mechanism (F1). The decomposition of biguanidinium diperchlorate is exothermic and very rapid. Table 1 summarizes the TG data for 17 experiments in which the heating was varied and shows the important parameters noted in Fig. 1 for each experiment. The final column in this table indicates if the run was included in the kinetic analysis. An examination of the results for which a kinetic analysis was not possible indicates that the amount of material used in three instances was too small to give accurate results. The sample containing 2.09 mg for which the kinetic analysis was also not possible was a TG run where an explosion occurred, possibly resulting in mechanical mass loss. The belief for an explosive event is based on the time versus temperature plot, Fig. 2, which shows a deviation from a constant heating rate, consistent with those found in larger examples that produced a green flash. The temperature data is retained, however, in Table 1 as the characteristic stages in the sequence of events can still be recognized.

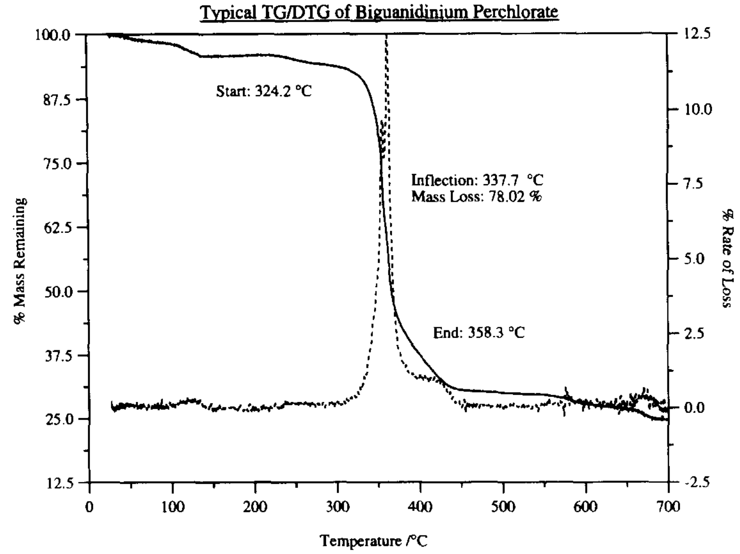

Fig. 1. TG/DTG plot showing the typical decomposition.

Table 1
Analysis of the main decomposition event

Mass/mg	Rate/ K min^{-1}	Start/K	Inflect./K	End/K	% Loss	Kinetic Analysis
2.18	1	288	310	362.7	77.29	Y
1.77	2	297	314	344	69.7	N
1.85	3	295	317	343	73.2	Y
2.45	4	301	314	333	70.72	Y
2.24	5	343	358	377	66.1	Y
2.46	6	324	338	358	78.02	Y
3.07	7	348	366	392	70.13	Y
2.53	8	316	331	350	69.86	Y
1.85	9	302	317	346	66	N
2.17	10	311	324	343	70.64	Y
1.98	10	321	336	359	64.85	Y
2.76	10	355	375	399	70.04	Y
2.05	20	348	360	361	76.39	Y
2.01	20	304	320	342	69.4	Y
2.09	30	349	360	367	83.37	N
1.46	30	318	334	352	67.35	Y
1.47	40	377	388	399	72.8	N

An examination of Fig. 1 shows that the main step is preceded by an initial loss of volatile material. This is the loss of adsorbed water, which accounts for a mass loss of about 10% for each sample.

The second step is a decomposition where the data fits a first-order (F1) mechanism. It is postulated that this mechanism changes at the maximum in the DTG trace

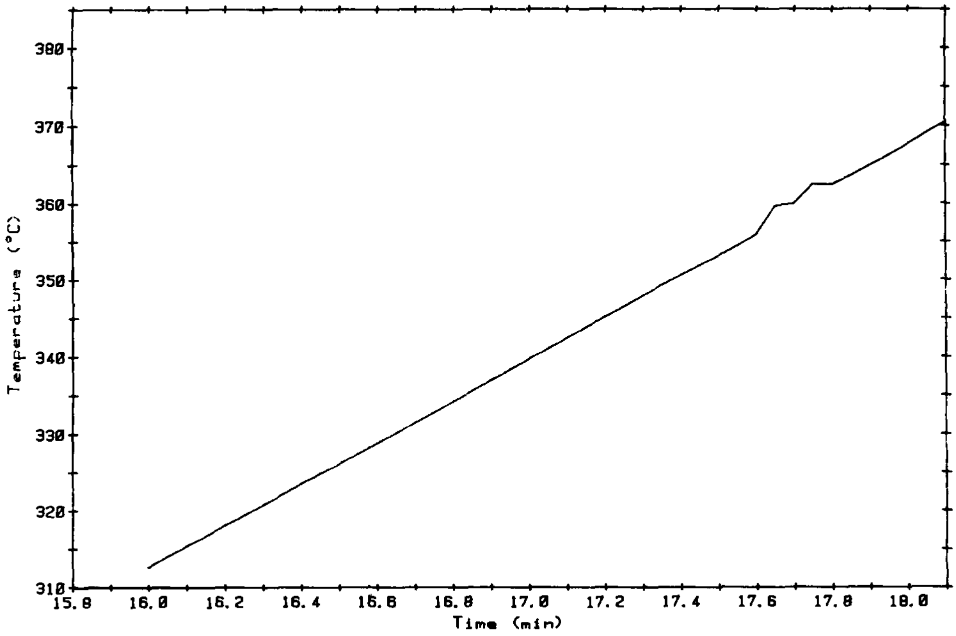

Fig. 2. Temperature versus time plot for 2.09 mg sample heated at 30 K min^{-1}.

(identical with the point of inflection in the TG curve). A third stage of the decomposition is continued decomposition after the point of inflection. This cannot be modelled with the F1 mechanism. These two stages account for a loss of about 70–80% of the sample (depending on the initial mass and the heating rate). In both stages the kinetic analysis shows a massive pre-exponential factor and a large activation energy (see next section for details).

It is likely there is fourth decomposition stage around 650°C. However, this trace only appeared on the slow heating rate experiments and there was insufficient data to analyze it properly. It typically accounted for 10% of the mass loss.

The mass spectrometry data was used to try and obtain a mechanism for the decomposition. A rising temperature direct insertion probe experiment was performed on a sample of biguanidinium diperchlorate. The data collected from the mass spectroscopy is shown in Figs. 3–6. To begin with, water, nitrogen and oxygen were detected from the sample. This was assumed to be adsorbed gas. Then, the most obvious feature of the mass spectrum of biguanidinium diperchlorate is the non-molecular ion peak of $m/z = 126$. This corresponds to a melamine radical ion ($[C_3N_6H_6]^+$). This is not unexpected and this type of rearrangement has been seen before [4]. The mass spectrum of melamine was also obtained. This was considered necessary to ensure that the biguanidinium diperchlorate spectrum was not going to simply be the decomposition of melamine. Melamine shows several peaks in its decomposition. These were compared against the biguanidinium perchlorate data.

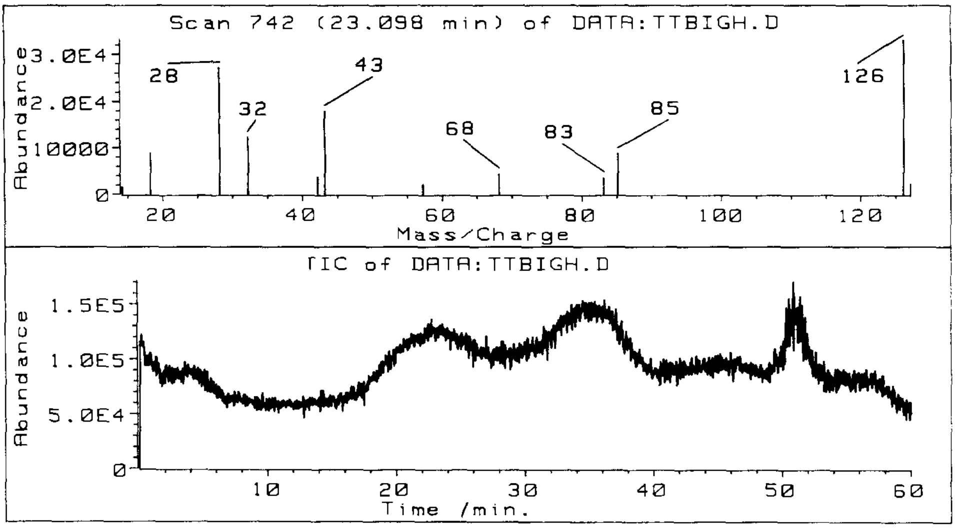

Fig. 3. Mass spectra of biguanidinium perchlorate after 23 min.

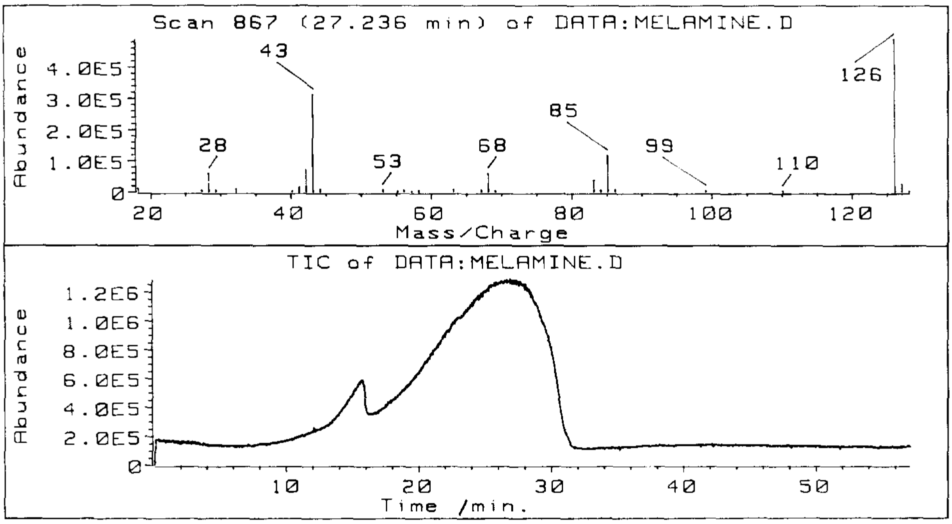

Fig. 4. Mass spectra of melamine after 27 min.

Early on (23 min, Fig. 3), the biguanidinium diperchlorate data showed essentially the same major peaks as pure melamine (Fig. 4), with some additional lower mass peaks corresponding to air and water. However, as the temperature at the dip probe continued to rise (35 min, Fig. 5), a number of additional peaks appeared in the spectra produced, and some peak relative intensities changed significantly compared to

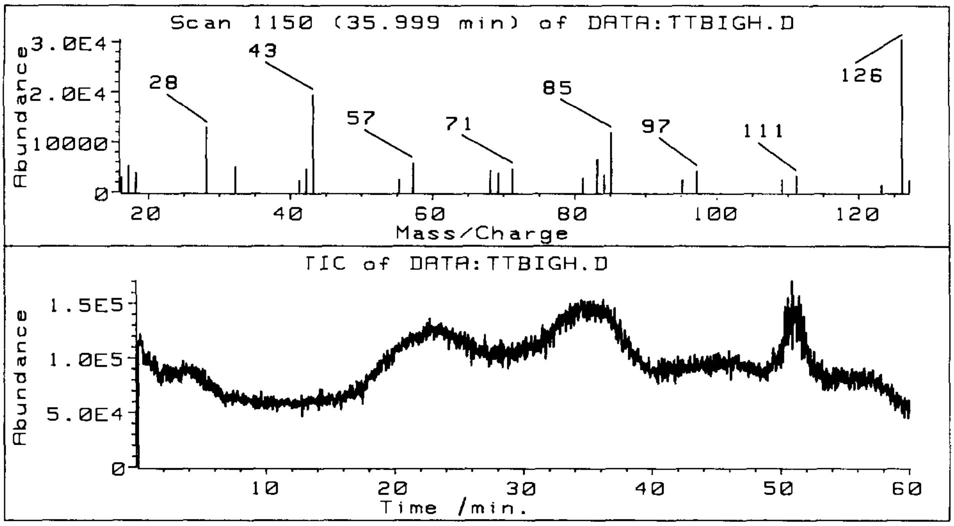

Fig. 5. Mass spectra of biguanidinium perchlorate after 35 min.

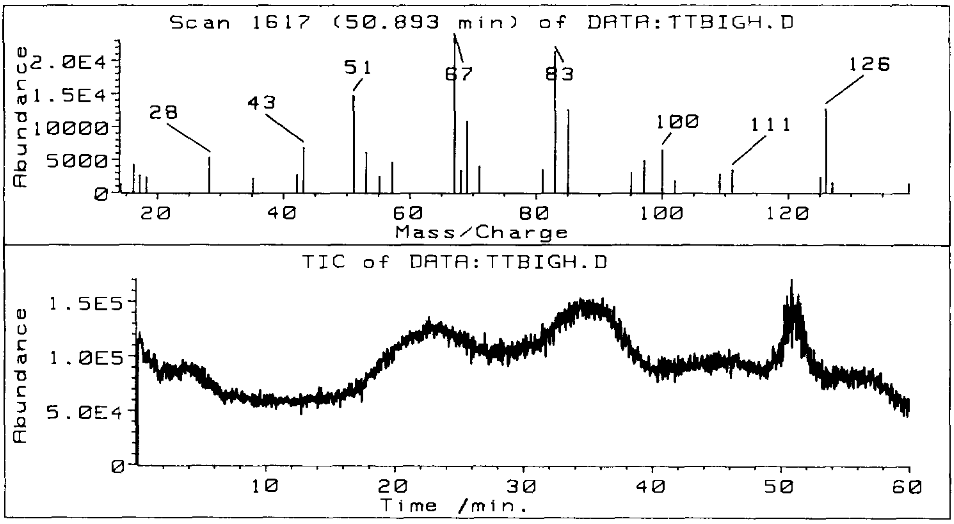

Fig. 6. Mass spectra of biguanidinium perchlorate after 50 min.

melamine. These changes were assumed to be due to the biguanidinium ion and not some more obscure rearrangement. The familiar chlorine peak pair was not seen at all. The peaks that did not appear in melamine or were significantly enhanced compared to melamine at 35 min were 32, 57, 84.

At the final peak in the total ion count (50 min, Fig. 5) an *m/z* peak of 102 was observed. This peak was not found at all in the melamine spectra, and we believe that this is the biguanidinium ion. It appears to decompose by initially losing pairs of hydrogen atoms and then an amine group with mass losses of 2 and 15. The peak sizes suggest that the hydrogen atoms are lost first. Peak 67 which is the most abundant at this time was seen to build slowly over the course of the experiment. There are many speculative structures that could be drawn for this, but it seems nonsensical to choose one over another. It should be noted that small peaks were seen at 137 and 153, suggesting that the melamine radical is formed from a less stable higher molecular weight ion.

4. Kinetic analysis

The procedure chosen to identify a kinetic mechanism was based on the fit of the data to the mechanism selected. When two mechanisms gave similar fits to the data (based on the correlation coefficient) the simpler mechanism was preferred. No one mechanism appears to fit all data over all the heating rates. The mechanisms investigated are listed by Dollimore and Reading [5] and the differential method of calculating the specific reaction rate was used. When the two mechanisms gave similar fits to the data (based on the correlation coefficients for the Arrhenius plots of log k against $1/T$) the simpler mechanism was preferred [6]. The main decomposition event can be split into two parts. The division between these two mechanisms can be approximated to the maximum in the DTG trace. This was done for all the data, and was not always successful, but it worked well enough for most of the samples. The reason why some of the data was not subjected to a kinetic analysis (see Table 1) has already been explained. Some data in the kinetic analysis fitted to the F1 mechanism had a correlation coefficient. The mechanism that best fitted the data up to the point of inflection (as noted in the TG trace) was found to be an F1 mechanism with a large pre-exponential factor and a large activation energy. The average correlation coefficient of the data fitted to the F1 mechanism was 0.977. The slower rate data fitted the F1 mechanism significantly less well than the more rapidly heated data. Values for the activation energy and pre-exponential factor for each run were evaluated and tabulated (Table 2). A compensation plot (Fig. 7) shows a linear relationship which could be interpreted as indicating that the mechanisms are related [7]. The occurrence of two or more kinetic models of decomposition has been previously noted [8–10]. The reason is that any change in the morphology of a solid material, e.g. abrupt changes in form, changes in surface area, or as in this case changes caused by explosions, must result in corresponding changes in the kinetics, especially if they are based on the models of an altering reaction interface. A further reason exists in extremely exothermic reactions, namely that the transfer of heat from the highly energetic processes might be reflected in the kinetic analysis. However, this was thought to be a significant contribution only after the inflection temperature and was one of the considerations why the kinetic analysis was not progressed beyond the DTG temperature. The point of inflection noted in Table

Table 2
Results of kinetic analysis using F1 mechanism

Rate/K $\min^{-1}$	ln A	E_a/ (kJ mol^{-1})	Correlation
1	51	243.5	0.919
3	60	275.6	0.944
4	116	534.1	0.989
5	90	439.3	0.967
6	120	567.7	0.986
7	84	409.8	0.907
8	94	437.3	0.993
10	78	400.7	0.994
10	110	513.7	0.981
10	120	552.4	0.988
20	100	450.4	0.992
20	165	882.3	0.992
30	98	443.4	0.983

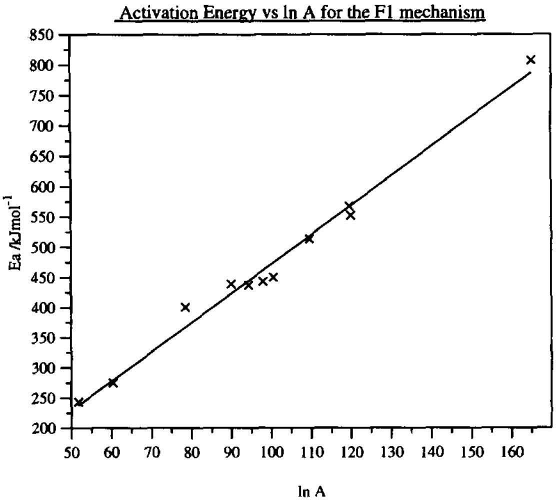

Fig. 7. The compensation plot for the data obeying the first-order (F1) mechanism.

1 can be taken as the point where the F1 mechanism ended and some new mechanism began.

At faster heating rates, the correlation in the Arrhenius plots based on the F1 mechanism is generally higher than in the slower heating rate experiments. The mass spectroscopy data offer an explanation as to why this is so. Clearly biguanidinium diperchlorate at lower decomposition temperatures can rearrange to form a more stable product, melamine. Thus slow heating rates will allow a larger portion of the sample to rearrange without mass loss. Then, as the biguanidinium diperchlorate decomposes, this other material interferes with the F1 mechanism, promoting another. This explanation also has the advantage of simplicity, although it should be noted that the environment of the mass spectroscopy experiments is very different to those in the TG experiments.

References

[1] M.I. Fauth, Anal Chem., 32 (1960) 655.
[2] C. Manuelli and L. Bernardini, Brit. Pat. (1917) # 155, 627.
[3] W.W. Wendlandt, Thermochim. Acta, 70 (1983) 379.
[4] T.M. Grahek and P. Bukovec, Thermochim. Acta, 215 (1993) 241.
[5] D. Dollimore and M. Reading, in J.D. Wineforder, D. Dollimore and J.G. Dunn, (Eds.), Treatise on Analytical Chemistry, Part I, Vol. 13, 2nd edn., Thermal Methods, J. Wiley, New York, 1993, Chapter 1.
[6] X. Gao and D. Dollimore, Thermochim. Acta, 215 (1993) 47.
[7] M.E. Brown, D. Dollimore and A.K. Galway, in C.H. Bamford and C.F. Tipper (Eds.) Comprehensive Chemical Kinetics, Vol. 22 Elsevier, Amsterdam, 1980, p. 340.
[8] D. Dollimore, J. Dollimore and D. Nicholson in J.H. de Boer (Ed.), Proc. Fourth International Symposium on the Reactivity of Solids, Elsevier, Amsterdam, 1960, p. 627.
[9] D. Dollimore and D. Tinsley, J. Chem. Soc. A, (1971) 3034.
[10] D. Dollimore, J. Therm. Anal., 39 (1992) 111.