Propellants, Explosives, Pyrotechnics *10*, 39–42 (1985)

Thermal Degradation of some Azines

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Thermischer Abbau von Azinen

Die thermische Charakterisierung von Tetraformaltrisazin und Formalazin wurde zum ersten Mal durchgeführt unter Einsatz der Differentialthermoanalyse, der Thermogravimetrie und der Massenspektrometrie. Über die kinetische Analyse des Abbaus jeder dieser Komponenten und den Einfluß der umgebenden Atmosphäre auf den Abbau wird berichtet. Abbaumechanismen werden postuliert. In Anlehnung an die Werte der Aktivierungsenergie und unterstützt durch Ergebnisse der massenspektrometrischen Untersuchungen wird festgestellt, daß die 2. Stufe des thermischen Abbaus von Tetraformaltrisazin und Formalazin in inerter Atmosphäre der Aufspaltung der N–N Bindung zugeschrieben werden kann. Die Zersetzungswärme von Tetraformaltrisazin und Formalazin wird bestimmt durch Differentialkalorimetrie. Die erhaltenen Werte sind 360,4 ± 0,5 cal/g bzw. 105,8 ± 0,7 cal/g.

Décomposition thermique des azines

On a étudié pour la première fois le comportement thermique de la tétraformaltrisazine et de la formalazine par analyse thermique différentielle, par thermogravimétrie et par spectroscopie de masse. On décrit la cinétique de la réaction de décomposition de ces produits et l'influence qu'exerce l'atmosphère environnante sur cette décomposition. On établit certaines hypothèses concernant les mécanismes de décomposition. Compte tenu des valeurs de l'énergie d'activation et des résultats de l'analyse des produits de décomposition par spectrométrie de masse, on constate que la deuxième phase de la décomposition thermique de la tétraformaltrisazine et de la formalazine en atmosphère inerte peut être attribuée à l'ouverture de la liaison N-N. La chaleur de décomposition de la tétraformaltrisazine et de la formalazine est determinée par calorimétrie différentielle. Les valeurs respectives sond 360,4 ± 0,5 cal/g et 105,8 ± 0,7 cal/g.

Summary

The thermal characteristics of tetraformaltrisazine and formalazine were studied for the first time using differential thermal analyser, thermogravimetric analyser and mass spectrometer. Kinetic analysis of the degradation of each of these compounds and the effect of enveloping atmosphere on the degradation are reported. Degradation mechanisms have been postulated. Based on values of activation energy and supported by evidences made available by mass spectrometric studies it has been concluded that the second stage of thermal degradation of tetraformaltrisazine and formalazine in inert atmosphere may be ascribed to N–N bond rupture.

The heats of degradation of tetraformaltrisazine and formalazine were determined by differential scanning calorimeter. The values obtained are + 360.4 ± 0.5 cal/g and + 105.8 ± 0.7 cal/g respectively.

1. Introduction

Tetraformaltrisazine is an interesting compound from the point of view of its use as an efficient fuel in hybrid propellant systems(1). Formalazine, a white amorphous polymeric material which has some similar structural features as that of tetraformaltrisazine may also be expected to find use as a good fuel. These compounds may also be used in explosive compositions, solid propellants etc. to modify the performance. The importance of these compounds being such, it would be of interest to study their degradation characteristics. It is the purpose of this investigation to shine light on these aspects of the materials.

2. Experimental

2.1. Preparation of materials

Tetraformaltrisazine (TFTA, $C_4H_{12}N_6$) and formalazine (FA, $C_2H_4N_2$) were prepared by the reaction between hydrazine and formaldehyde as described in literature(1). TFTA was recrystallised from water, washed with water and alcohol and dried. Since FA is insoluble in the common solvents, it was used after washing several times with water and drying under vacuum. The infrared absorptions of these compounds were identical to the reported ones(1).

2.2. Apparatus

Differential thermal analysis (DTA) and thermogravimetry (TG) traces were obtained on a DuPont 900 differential thermal analyser and a DuPont 950 thermogravimetric analyser, the latter being a plug-in module for the 900 console. A Hitachi Perkin Elmer RMU-6 H mass spectrometer was used to analyse the degradation products of TFTA and FA. A Perkin-Elmer differential scanning calorimeter DSC-IB was employed to measure the heat of degradation. Changes in the physical state of the compounds as they were heated on a slide using a Mettler FP 2 system were observed under a microscope (Bausch & Lamb Inc.)

3. Results and Discussion

DTA and TG traces of TFTA in nitrogen, air and oxygen atmospheres were obtained at atmospheric pressure. Typical traces in nitrogen are shown in Fig. 1.

The DTA trace showed an endotherm at 183 °C. This may be due to degradation with melting. The white crystals turned to a yellowish fluid as seen under a hot-stage microscope. The initial deflection point in the TG curve associated with the degradation is at 145 °C. The temperature at 50% weight-loss is 220 °C. When these experiments were carried out under air or oxygen, no significant difference in the degradation temperatures was observed. In these atmospheres the endotherm in the DTA trace appeared at 180 °C. Similarly the temperature corresponding to inflexion point was 144 °C and the temperature at 50% weight-loss was 219 °C, but the shapes of the TG curves were exactly identical to that obtained when the experiment was carried out in a flowing nitrogen atmosphere.

0721-3115/85/0204-0039$02.50/0

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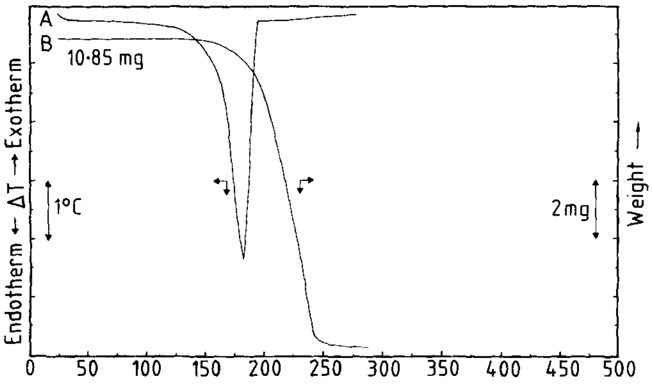


Figure 1. Typical DTA and TG traces (A and B respectively) of TFTA in a flowing nitrogen atmosphere.

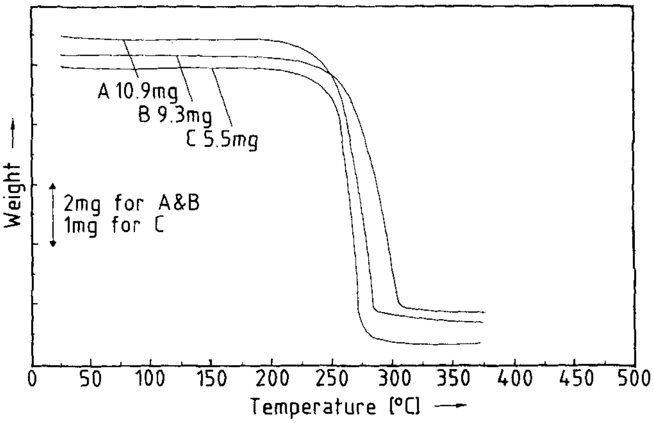


Figure 3. Typical TG traces of FA in: (A) flowing nitrogen atmosphere, (B) flowing air atmosphere, (C) flowing oxygen atmosphere.

The DTA study of FA in different atmospheres of gases (see Fig. 2) yielded interesting results. Unlike in the case of TFTA, there were notable differences among the thermal characteristics of FA in various atmospheres. In nitrogen atmosphere the base line in the DTA trace of FA starts sloping upwards, an "extherm" is shown up with peak temperature at 246 °C and an endotherm is recorded immediately following it, with its peak at 258 °C. This sloping of base line or "exotherm" may be due to heat capacity transition and/or some exothermic reaction occurring in the sample. An exothermic reaction may be explained in terms of oxidative degradation due to the presence of very small amounts of air in the voids of the sample or due to adsorbed air which might not have been removed by flushing with nitrogen. The endotherm may be ascribed to degradation with melting, as can be observed under a hot-stage microscope. However, in the more complex process of thermooxidative degradation, the initial stages are more exothermic since the peak height and area of the "exotherm", just preceding the endotherm, increase when the sample is enveloped by air and this increase is more prominent if the enveloping atmosphere is oxygen. The procedural initial decomposition temperature (T_i) and the peak temperature (T_{max}) of the "exotherm" are T_i = 185 °C (nitrogen), 160 °C (air) and 150 °C (oxygen) and T_{max} = 246 °C (nitrogen), 225 °C (air) and 218 °C (oxygen). These values do show the effect of the surrounding atmosphere on the degradation of FA. Also, the endotherm gets shifted to lower temperatures with a change in the atmosphere as shown by the peak temperatures, 259 °C (nitrogen), 238 °C (air) and 228 °C (oxygen).

The TG traces of FA in various atmospheres (see Fig. 3) also show the same trend in degradation characteristics. Whereas the inflexion point remained the same at 200 °C irrespective of the gas enveloping the sample, the temperatures at 50% weight-loss were 287 °C (nitrogen), 270 °C (air) and 265 °C (oxygen).

From the results, as outlined in the above paragraphs, it seems that TFTA is thermally less stable than FA. It further seems that the degradation of FA is very much influenced by the atmosphere while in the case of TFTA the effect is negligible. With a view to understanding the energetics and mechanism of degradation of these compounds, the kinetic studies and mass spectrometric investigations of these compounds were undertaken.

The kinetics of thermal degradation of TFTA and FA were followed by dynamic thermogravimetry at a heating rate of 8 °C/minute. The constant flow rate of gas viz., 250 ml/min was

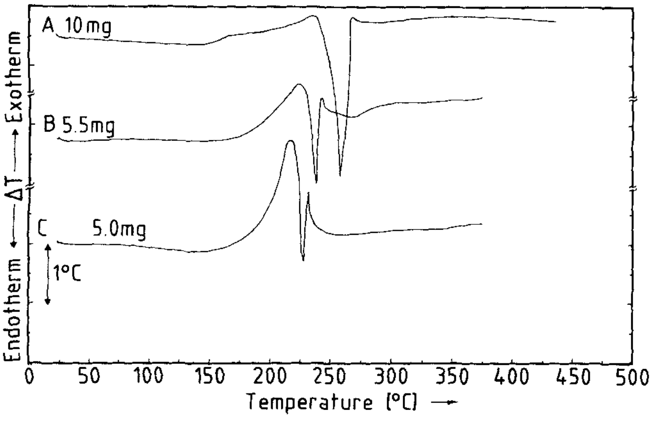


Figure 2. Typical DTA traces of FA in: (A) flowing nitrogen atmosphere, (B) flowing air atmosphere, (C) flowing oxygen atmosphere.

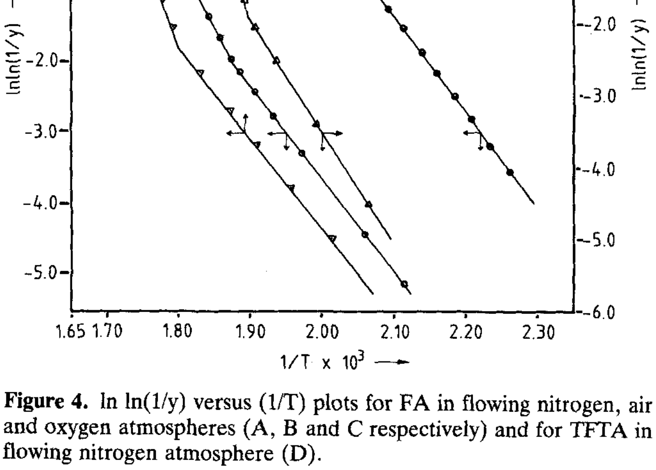


Figure 4. ln ln(1/y) versus (1/T) plots for FA in flowing nitrogen, air and oxygen atmospheres (A, B and C respectively) and for TFTA in flowing nitrogen atmosphere (D).

Table 1. Kinetic Results

Material	Temperature range [°C]	Activation energy, E [kcal/mol]	α value to which E is applicable
TFTA	170–225	26.7	<0.58
(flowing nitrogen	225–245	38.5	>0.58
FA	200–260	25.7	<0.10
(flowing nitrogen)	260–295	37.6	0.10–0.73
	295–305	59.6	>0.73
FA	200–250	25.8	<0.12
(flowing air)	260–280	54.6	0.2–0.72
FA	211–253	31.1	<0.10
(flowing oxygen)	253–275	79.5	0.10–0.94

maintained in all the experiments. Since TG experiments on TFTA yielded almost super-imposable curves in nitrogen, air and oxygen atmospheres, the kinetics analysis was done only in the case of experimental results obtained on TFTA in nitrogen atmosphere. However, in the case of FA, since the TG curves were remarkably different in the various atmospheres, the kinetics were studied in nitrogen, air and oxygen atmospheres separately. The kinetic analysis of the TG data was done by Broido's method(2). The ln ln(1/y) versus 1/T plots (Fig. 4) show that the energetics of the degradation do not remain the same throughout the reaction but increase as the reaction proceeds. The values of activation energy obtained are listed in Table 1.

Up to a fractional degradation, α of 0.58 TFTA degrades with an activation energy (E) value of 26.7 kcal/mol and beyond α, 0.58 E is raised to 38.5 kcal/mol. Similarly FA also degrades with different values of E for the different stages of the reaction, as shown in Table 1. It can be seen that in the case of both TFTA and FA in nitrogen atmosphere, the values of activation energy needed for the initial stage of the reaction are close to each other though the fraction of degradation to which these apply vary. While in the case of TFTA E applies up to $\alpha = 0.58$, in FA it applies only up to $\alpha = 0.1$. The rate-determining reaction in the initial stage of degradation of TFTA and FA, however, seems to be the same.

Considering the major portion of degradation (by way of weight-loss) of FA in nitrogen atmosphere with an E of 37.6 kcal/mol, it seems that this value of E is very close to the value of E obtained for the degradation of TFTA beyond $\alpha = 0.58$. Thus it looks as though the slowest step in each stage of the complex degradation process of TFTA and FA in flowing nitrogen atmosphere is identical. However, it is very difficult to assign the different values of activation energy to different particular processes with certainty although the bond energy value of 38 kcal/mol for N–N bond(3, 4) may tempt one to suggest that the rate-determining step of the second stage of the degradation of TFTA and FA may be nitrogen-nitrogen bond rupture.

FA is a polymeric compound. The complexity of degradation may increase with the complexity of the molecule. The general classification of the mechanism of degradation of polymers according to Rabinovitch(5) is as follows:

(a) Scission of bonds
  - scission at random
  - scission of weak bonds

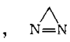
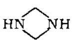
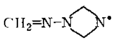
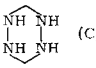
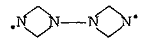
(b) Reverse polymerization
  - end initiation and unzipping
  - random initiation and unzipping.

Since value of activation energy for FA changes from non-oxidative to oxidative atmosphere, it is likely that the mechanism of degradation may not involve a reverse polymerization process but may involve scission of bonds. Thus bond rupture and probably also the formation of free radicals may be taking place in the degradation of FA. Mass spectrometric investigations, the results of which are given in some of the proceeding paragraphs, seem to support this view.

Comparing the activation energies for the thermal degradation of FA in different atmospheres, it is seen that the values of E for the major process (on the basis of weight-loss) in the degradation in nitrogen, air and oxygen atmospheres increase in this order (Table 1). This observation is difficult to be explained if the particular slowest process in the major weight-loss region is assumed to be the same. Probably the mechanism of the rate-determining step in the major reaction is influenced by the atmosphere surrounding the sample and/or may not be the same in the various atmospheres. This could be the case if diffusion of the initial reaction products out of the sample and/or the secondary reactions either among the reaction products themselves or with the enveloping gas (applicable only to non-inert gases) could be playing an important role in the degradation of FA.

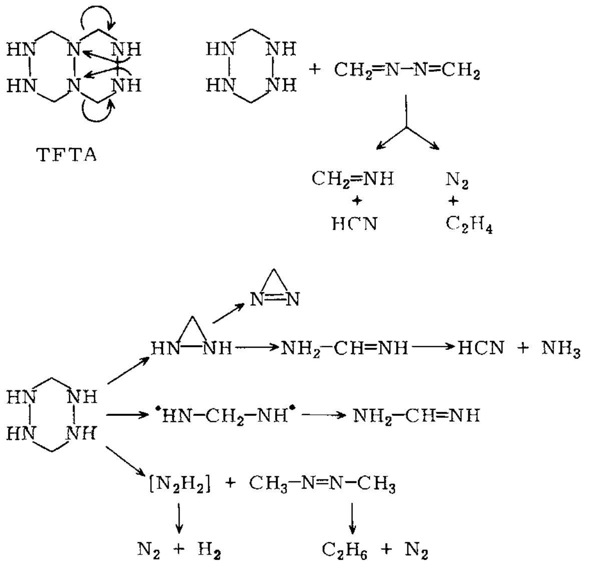
The results of the studies on the degradation of TFTA at 180 °C and of FA at 260 °C (these are the optimum temperatures at which the materials under high vacuum degraded yielding detectable amount of gaseous products) employing mass spectrometer are listed in Table 2.

Table 2. Mass Spectral Data

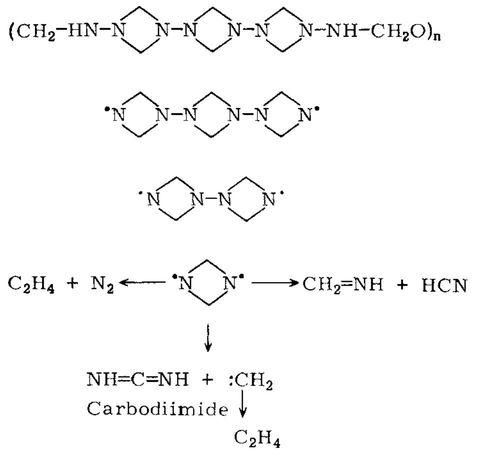
m/e	Fragments	Relative intensities TFTA	FA
12	C	0.3	0.5
14	N, CH_2	1.6	3.6
15	CH_3, NH	1.2	2.5
16	NH_2, CH_4	0.8	0.6
17	NH_3, OH	1.1	0.8
18	H_2O	0.7	0.5
27	HCN	2.7	10.6
28	N_2, C_2H_4, $\cdot CH{=}NH$, CO	12.5	41.8
29	$CH_2{=}NH$	3.3	5.8
30	N_2H_2, C_2H_6	5.8	4.1
32	N_2H_4	2.6	0.5
41	CH_3CN	0.7	2.4
42	$NH{=}C{=}NH$, $CH_2{=}N{\rightarrow}N$, 	3.1	10.0
43	HN_3, 	3.4	4.0
44	$NH_2{-}CH{=}NH$, CO_2, 	6.5	3.3
56	$CH_2{=}N{-}N{=}CH_2$, 	3.7	24.4
57	$CH_2{-}N{=}CH{-}NH_2$,	–	9.1
58	$CH_3{-}N{=}N{-}CH_3$ 	0.4	1.1
69		–	2.3
70		–	2.3
83		–	2.9
84		–	2.0
88	 $(C_2H_8N_4)$	7.9	–
112		–	3.1
168		–	1.7

The various m/e values have been ascribed to the presence of species or fragments formed by several available sequences of reactions.

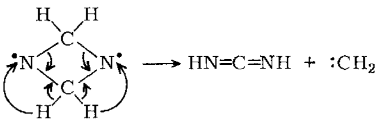
The important degradation products of TFTA seem to be nitrogen, ethylene, $C_2H_8N_4$, diaziridine and/or NH_2–CH=NH, 2,3-diazabutadiene-1,3 (CH_2=N–N=CH_2), ethane, hydrazine and some hydrogen cyanide. Based on the formation of these products and assuming intramolecular H rearrangement a scheme of degradation has been outlined.



Similarly FA undergoes degradation to yield a variety of products. The most important of them seem to be nitrogen, ethylene, 2,3-diazabutadiene-1,3 or $C_2H_4N_2$, carbodiimide, hydrogen cyanide etc. Based on the formation of these compounds, mechanisms for the degradation of FA has been postulated. If C–N bond scission alone is operative in the degradation, the formation of various species as detected by mass spectrometer is difficult to be explained. But N–N bond rupture seems to explain the formation of all important products. The scheme of degradation is as given below:



The formation of carbodiimide can be visualised as:



The probability of cleavage of a bond is related to the bond strength. Comparing the N–N and C–N bonding energies as reported in literature(3, 4) (these values may be different from the actual energy of the bonds in the molecules of the compounds under study depending upon the atoms/groups attached to N–N and C–N. However, they are good enough for comparison purposes) it seems that the N–N bond is more easily cleaved than the other. There is mass spectrometric evidence for the N–N bond cleavage as shown by the presence of species which could not have formed but for the N–N bond scission. This seems to support the observation made on kinetic results that the second step in the thermal degradation of TFTA and FA in non-oxidizing atmospheres may be the rupture of N–N bond. However, in the more complex reactions that occur in an oxidizing atmosphere in the case of FA, N–N bond rupture may not be the rate-determining step. On the other hand it may be the oxidative attack on one of the bonds or other processes as described earlier. While the chances of an oxidative attack to be the rate-determining step during some stage in the thermal decomposition of FA in air, and oxygen cannot be ruled out, it does not seem to be the slowest step in the major portion of the degradation since in that case values of E in air and oxygen should have been more or less the same, which is not the case. Diffusion of reaction products or secondary reactions could thus be the rate-determining step in the major portion of the thermal decomposition of FA in air and oxygen.

The heats of degradation of TFTA and FA as determined by differential scanning calorimeter are + 360.4 ± 0.5 cal/g and + 105.8 ± 0.7 cal/g. The degradation of TFTA is much more endothermic than that of FA.

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Acknowledgement

The author wishes to express his appreciation to the authorities of the University of Houston, Houston, Texas, USA for the use of the various instruments, during his stay at the University.

(Received January 24, 1984; Ms 12/84)