Thermochimica Acta, 89 (1985) 11–26
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HEATS OF DECOMPOSITION, COMBUSTION AND EXPLOSION OF NITROCELLULOSES DERIVED FROM WOOD AND COTTON

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(Received 27 December 1984)

ABSTRACT

Heats of decomposition, explosion and combustion of nitrocellulose (NC) fibers derived from wood (three samples) and cotton (four samples) were measured using differential scanning calorimetry (DSC) and bomb calorimetry. The nitrogen content of the fibers ranged from 12.6 to 13.5%. A procedure for obtaining accurate and precise average heats of decomposition (standard deviation from the mean of about 2%) is proposed. A limited number of measurements were also performed with DSC, using NC films cast from acetone, tetrahydrofuran and ethyl acetate. Average heats of decomposition, explosion and combustion thus obtained are of the order of 2.0, 4.0 and 9.5 kJ g^{-1}, respectively. Degradation mechanisms are discussed in relation to the surrounding atmosphere of reaction, and as a function of the nitrogen content of the samples.

INTRODUCTION

The thermal decomposition of nitrocellulose (NC) has been studied for many years [1]. Wolfrom et al. [2] analyzed NC decomposition products by assuming that the thermally initiated rupture of the cellulose nitrate molecules gives a series of volatile species whose relative importance is inversely proportional to the pressure of the system. Using spectroscopic and gravimetric techniques, Phillips et al. [3] showed that the thermal degradation of NC follows, in first approximation, first-order kinetics with two or three branches, suggesting that a more complex reaction process might occur.

The analysis of the thermal decomposition of NC can also be carried out by differential scanning calorimetry (DSC). For example, House et al. [4] compared the decomposition of twelve commercial NC propellants using this method. He observed two different decomposition patterns for the same propellant, run in the same fashion. The first one is

$$\text{Propellant} \rightarrow \text{volatile products} + 12\text{–}16\% \text{ residue} \qquad (1)$$

while the second is

$$\text{Propellant} \rightarrow \text{volatile products} + 2\text{–}5\% \text{ residue} \qquad (2)$$

0040-6031/85/$03.30

His results indicate that there is no significant difference between the heats of decomposition of most propellants investigated which decompose according to eqn. (1). However, for some propellants, decomposition takes place by eqn. (1) or (2), with about equal frequency.

More recently, Pfeil and Eisenreich [5] studied the thermal decomposition of NC by thermogravimetric analysis, differential thermal analysis, and infrared and Raman spectroscopies. Their results revealed the presence of an initial autocatalytic decomposition of nitrate groups and an increase in carbonyl and hydroxyl groups up to a weight loss of 55%. Further decomposition turned out to be a second-order reaction, terminating in a charcoal-like residue.

To our knowledge, attempts have never been made to differentiate the thermal decomposition of NC derived from wood and from cotton. It is the purpose of this article to use a DSC apparatus to compare the heats of decomposition of seven NC fibers, derived from wood and cotton. The NC fibers investigated had various nitrogen contents ranging from 12.6 to 13.5%. Heats of decomposition of the same NC samples, cast from acetone, tetrahydrofuran and ethyl acetate, were also measured. Moreover, heats of explosion and combustion were determined for all NC fiber samples using bomb calorimetry. Degradation mechanisms are finally discussed in relation to the surrounding atmosphere of reaction, and as a function of the nitrogen content of the samples.

EXPERIMENTAL

Sample preparation

Seven nitrocellulose samples have been used in the present study. Their main characteristics are given in Table 1. It should be noticed that the acronym NCW-1343 stands for a nitrocellulose (NC) derived from wood (W) and containing 13.43% of nitrogen; the acronym NCC-1350 stands for a nitrocellulose (NC) derived from cotton (C) and containing 13.50% of nitrogen; the other acronyms have a similar meaning.

The NC wet fibers were dried in a vacuum oven for several days at room temperature. NC solutions were prepared using distilled tetrahydrofuran (THF), spectroscopic grade acetone or ethyl acetate, with dry fibers, and films were cast thereof. In all cases, solvent evaporation was conducted at room temperature. The resulting films were removed from petri dishes, and dried in a vacuum oven until they reached constant weight.

DSC analysis

DSC measurements were conducted with a Perkin-Elmer DSC-1B apparatus at a heating rate of 20 K min^{-1}. The apparatus was calibrated with

TABLE 1

Nitrocellulose samples used

Sample	Country of origin	Cellulose source	% N	Molecular weight (GPC) (kg mol^{-1})		Remarks
				$\overline{M}_w$	$\overline{M}_n$	
NCW-1343	Canada	Wood	13.43	409	100	high grade (Grade B) woodpulp (Rayonier Q-LD) Expro Chemical Products Inc.
NCW-1342	Canada	Wood	13.42	405	117	high grade (Grade B) Expro Chemical Products Inc.
NCW-1262	Canada	Wood	12.62	342	145	Pyro (Grade A, Type I) woodpulp (Rayonier Q-LD) Expro Chemical Products Inc.
NCC-1350	U.S.A.	Cotton	13.50	323	103	high grade (Grade B) U.S. Army Ballistic Research Laboratories
NCC-1314	Canada	Cotton	13.14	360	163	Military Blend (Grade C, Type I) sheeted cotton linters (Buckeye Corp.) Expro Chemical Products Inc.
NCC-1274	Australia	Cotton	12.74	309	125	mechanically nitrated papered cotton linters (Shoalhaven) Mulwala Explosives Factory
NCC-1260	U.S.A.	Cotton	12.60	370	100	Pyro (Grade A, Type I) U.S. Army Ballistic Research Laboratories

respect to temperature and surface area with indium ($T_m = 429$ K and $\Delta H_m = 28.4$ J g^{-1}). An empty pan was used as the reference for all measurements. The surface areas were measured after transferring the decomposition curves and baselines from a chart paper to a microcomputer. The integration was carried out using 300 data points for each curve and Simpson's rule.

In the DSC experiment, we paid attention to the choice of a proper baseline since the NC decomposition thermograms are broad and a straight baseline may not be a proper choice [6,7]. We preferred to use the technique proposed by Duswalt [8] where, after the initial decomposition, the temperature of the sample is lowered and a second run is made under the same conditions. This method conducted to curved baselines, which we considered to be more appropriate than a straight line. The values of enthalpy of decomposition found by this method are quite different from those which were calculated using a straight baseline.

Typical DSC thermograms for NC are shown in Fig. 1. The exothermic decomposition peak is asymmetric with decomposition starting at about 450 K and finishing at about 530 K, with a maximum located at about 490 K.

However, the shape of the decomposition curves varies with operating conditions. For example, the way in which the sample is crimped is quite important. The standard crimping procedure recommended by the DSC manufacturer was found to be inefficient. It does not always give reproducible results: tight crimping may prevent an efficient purge by the nitrogen gas flowing through the calorimeter, hindering the escape of volatile species produced by the decomposition reaction.

Sammons [9] suggested punching holes in the capsule lid to control the escape of large amounts of decomposition gases. Ellerstein [10], on the other hand, placed the sample between two circular disks made of a fine mesh, inert metal screen, thus reducing the thermal gradients across the sample.

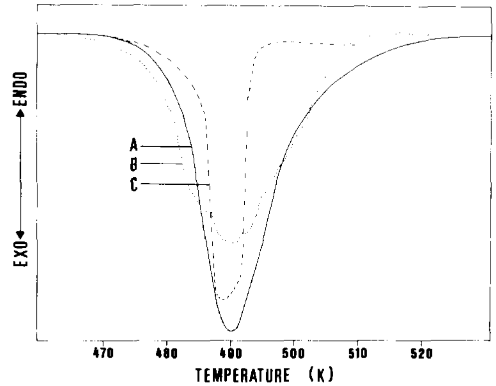


Fig. 1. DSC curves for the decomposition of NC fibers: (A) 1.0 mg; (B) 0.3 mg; (C) 2.0 mg of sample.

The method that we used is different but as efficient as those mentioned above. First, we crimped the NC samples in the usual manner with aluminum pan and cover. Then, the rim of the capsule was pinched with tweezers in a criss-cross way that left a clearance between the pan and the cover, enabling decomposition gases to escape easily. This operation left the bottom of the capsule uniform to allow a proper thermal contact between the sample holder and the capsule, and it led to decomposition curves free of irregularities.

Another important parameter to consider is the weight of the sample introduced into the capsule. Figures 1A, B and C were obtained with samples of 1.0, 0.3 and 2.0 mg of NC, respectively. With small amounts of sample (Fig. 1B), a poor contact between the capsule and the sample often seems to exist, leading to irregularities in the decomposition curve and to large fluctuations in values of the heat of decomposition. In addition, Fig. 1B is characterized by a width at half-height which is larger (about 19 K) than that measured for the regular curve shown in Fig. 1A (about 12 K).

With Fig. 1C, the reverse is observed: the width at half-height is smaller (about 6 K) than that found with Fig. 1A. The shape of curve C is related to the important quantity of NC inside the capsule. It is well known [11] that an explosive substance may encounter a transition from deflagration to detonation if it is confined in a closed vessel. This phenomenon results in a sudden increase of pressure and temperature inside the capsule. It is assumed in such cases that the electrical system of the DSC apparatus cannot respond fast enough to the significant amount of heat suddenly released, which generates a narrow decomposition curve. This phenomenon also results in heats of decomposition which are smaller than those found in Figs. 1A and B.

From the previous discussion, a standard experimental procedure was developed:

(1) the sample weight was always kept between 0.5 and 1.5 mg;

(2) the crimping of the sample was completed by the criss-cross pinching procedure described earlier;

(3) the sample capsule was placed in the DSC apparatus, brought rapidly to 390 K and equilibrated for 2 min;

(4) the DSC run was made at a heating rate of 20 K min^{-1}, from 390 to 550 K, under a nitrogen flow of 65 $\text{cm}^3\ \text{min}^{-1}$;

(5) after reaching 550 K, the system was rapidly cooled to 390 K and the equilibrium and heating cycles were repeated in order to determine the sample baseline.

With this procedure, only 6% of the curves recorded during this study [12] exhibited a decomposition pattern differing from that of Fig. 1A. These curves were excluded from the calculations of average heats of decomposition. This small percentage of rejected curves has to be compared to a value of 25%, obtained in a preliminary analysis, when using the standard procedure suggested by the DSC manufacturer and when the weight of the samples was not kept in the 0.5–1.5 mg range.

The use of this standard experimental procedure also favors an increase in precision. Thus, for NCC-1350 films cast in THF, a standard deviation from the mean of 1% was obtained whereas a value of 4% was previously calculated when our procedure was not followed thoroughly. This latter value is similar to the standard deviation values often reported in the literature for this sort of sample [4,13].

Bomb calorimetry

Heats of combustion and explosion were determined with a Parr calorimetric bomb [14], using an iron wire to initiate the combustion or explosion. High-purity benzoic acid was used to determine the heat capacity of the calorimetric system. Between 0.50 and 1.00 g of dried NC fibers were pressed into a pellet which was then introduced into the bomb. Combustion was carried out under 25 atm of oxygen, whereas explosion was provoked under 25 atm of nitrogen. Heats of combustion and explosion for each sample were calculated in the usual manner [14]. An average of five pellets were run for each sample and average values are reported here.

RESULTS

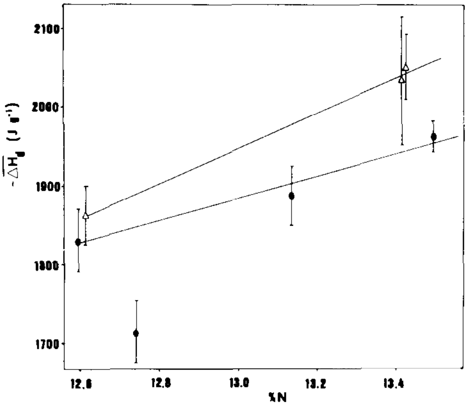
DSC analysis

Average heats of decomposition, obtained from the DSC measurements, are plotted against nitrogen content in Figs. 2–5. Each data point corresponds to an average of ten decomposition curves. A standard deviation from the mean was determined in each case, after having discarded the curves which differ from that described in Fig. 1A.

Average heats of decomposition for NC fibers range from 1711 to 2050 J g^{-1} (Fig. 2) whereas they range from 1812 to 2226 J g^{-1} for NC samples cast from solutions (Figs. 3–5). Precise values are obtained since standard deviations from the mean of about 2% are usually recorded. The method described above lowers the probability of getting decomposition curves differing from that described in Fig. 1A, without eliminating this possibility.

The accuracy of the results was checked by comparing average heats of decomposition for three series of fibers, each series being measured by two different operators. In each case, a good reproducibility was observed. Thus, for NCC-1314, two different operators obtained heats of decomposition of 1890 ± 38 and 1930 ± 19 J g^{-1}.

Figure 2 shows an increase in heats of decomposition of NC fibers derived from wood or cotton as a function of nitrogen content. A comparison of the



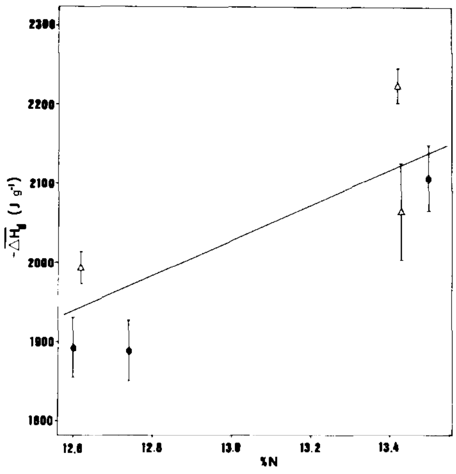


Fig. 2. Variation of the average heat of decomposition with nitrogen content: (△) NC fibers derived from wood; (●) NC fibers derived from cotton.

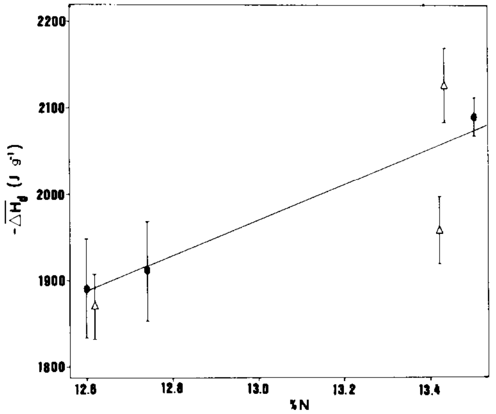
Fig. 3. Variation of the average heat of decomposition with nitrogen content for NC films cast from acetone: (△) NC derived from wood; (●) NC derived from cotton.

two types of NC fibers shows that the heats of decomposition are quite similar at low nitrogen contents. However, when the nitrogen content is increased, heats of decomposition obtained for NC fibers derived from wood are slightly higher than those measured for cotton. Figure 2 also shows that the average heat of decomposition of sample NCC-1274 is lower than those obtained from other samples. This behavior may be due to the origin of this sample, which is very different from that of all the other samples investigated, as shown in Table 1. In addition, the average heat of decomposition of sample NCC-1314 is intermediate between those of samples NCC-1260 and NCC-1350, as expected since this is a blend prepared from two NC having lower and higher nitrogen contents.

NC films cast in acetone and THF (Figs. 3 and 4) also exhibit an increase in heats of decomposition with nitrogen content, despite some scattering of the results at high nitrogen contents. In the case of films cast in ethyl acetate (Fig. 5), there is a slight increase in heats of decomposition with nitrogen content for NC derived from wood whereas there is almost no variation in heats of decomposition for NC derived from cotton.

This unique behavior of NC samples cast in ethyl acetate could enable cotton samples to be differentiated from wood samples, at a given nitrogen content, since these two types of NC exhibit significantly different heat of decomposition values.

Figures 3 and 4 show that films cast in acetone have average heats of decomposition slightly higher than those obtained using films cast in THF. Average heats of decomposition calculated for these films (in acetone and



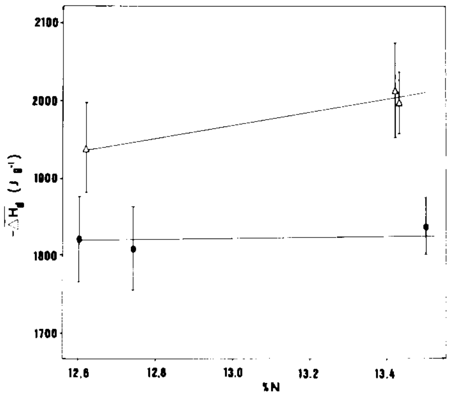


Fig. 4. Variation of the average heat of decomposition with nitrogen content for NC films cast from THF: (△) NC derived from wood; (●) NC derived from cotton.

Fig. 5. Variation of the average heat of decomposition with nitrogen content for NC films cast from ethyl acetate: (△) NC derived from wood; (●) NC derived from cotton.

THF) vary between 1870 and 2226 J g^{-1} while the variation observed for NC dried fibers is between 1711 and 2050 J g^{-1}. Therefore, acetone and THF lead to a slight increase of the average heats of decomposition for the NC samples. On the other hand, NC films prepared from ethyl acetate (Fig. 5), derived from wood or from cotton and having a low nitrogen content, show the same average heats of decomposition as those obtained for NC dried fibers of the same type and nature. However, NC films prepared from ethyl acetate, derived from cotton and having a high nitrogen content, show lower average heats of decomposition than the corresponding NC dried fibers.

It is then possible to change the decomposition behavior of NC slightly by exposing them to solvents which are likely to be retained to various degrees by the NC molecules.

Bomb calorimetry

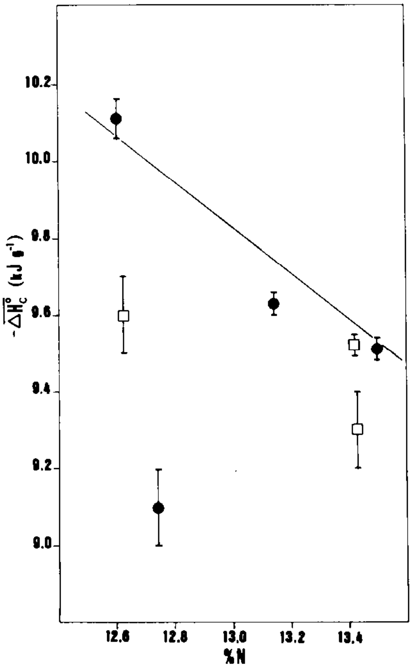
Average heats of combustion for the NC samples vary between 9.0 and 10.2 kJ g^{-1}. Figure 6 shows a small decrease of these values as a function of nitrogen content, particularly for NC samples derived from cotton. However, sample NCC-1274 shows an average heat of combustion significantly lower than those of the other cotton samples investigated. This sample also showed a low average heat of decomposition (Fig. 2) as compared to the other NC samples, which was assigned to the origin of the sample which is quite different from that of the others.

The average heats of combustion of NC samples derived from wood are slightly lower than those obtained for NC samples derived from cotton: the difference between these two series of results varies from 0.2 to 0.5 kJ g^{-1}. These results are also in good agreement with data taken from the literature [15], which are given in Fig. 6 by the straight line.

The average heats of explosion for the NC samples vary between 3.6 and 4.3 kJ g^{-1}. Figure 7 shows an increase of these values as a function of nitrogen content. This behavior is in good agreement with literature data [16,17] where values ranged from 3.6 to 4.2 kJ g^{-1} for NC samples having a nitrogen content varying between 12.62 and 13.45%. In addition, the average heats of explosion obtained with NC samples derived from cotton are higher than those measured for NC samples derived from wood, at nitrogen contents higher than 13.0%.

DISCUSSION

Figure 8 compares the average heats of decomposition $(\overline{\Delta H^0_d})$, explosion $(\overline{\Delta H^0_e})$ and combustion $(\overline{\Delta H^0_c})$ of NC fibers derived from wood and cotton. Average heats of decomposition are of the order of 2.0 kJ g^{-1} as compared to 4.0 and 9.5 kJ g^{-1} for the average heats of explosion and combustion,



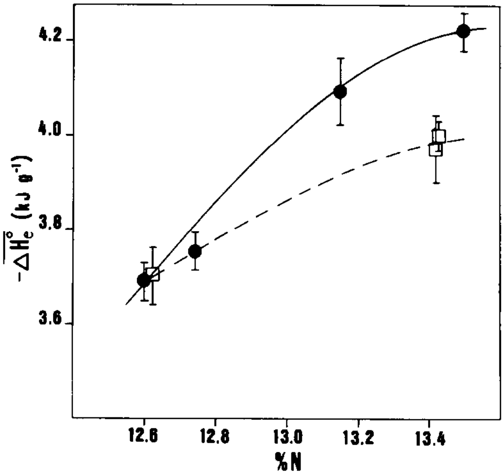


Fig. 6. Variation of the average heat of combustion with nitrogen content: (□) NC fibers derived from wood; (●) NC fibers derived from cotton. The straight line is taken from ref. 15.

Fig. 7. Variation of the average heat of explosion with nitrogen content: (□) NC fibers derived from wood; (●) NC fibers derived from cotton.

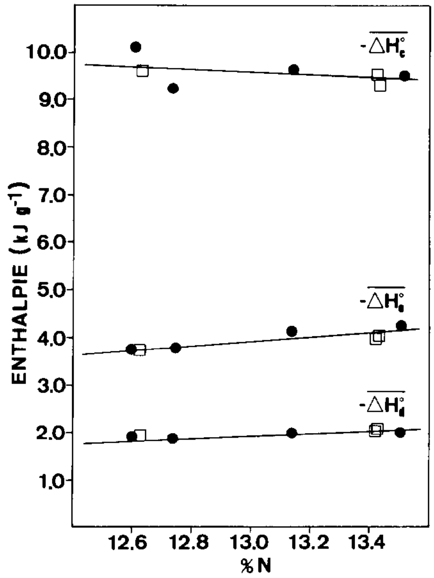


Fig. 8. Comparison between the average heat of decomposition ($-\overline{\Delta H_d^0}$), the average heat of explosion ($-\overline{\Delta H_e^0}$) and the average heat of combustion ($-\overline{\Delta H_c^0}$) as a function of nitrogen content: (□) NC fibers derived from wood; (●) NC fibers derived from cotton.

respectively. The important gap between these three energy levels can be explained as follows.

Any substance with an empirical formula $C_aH_bO_cN_d$ can decompose through oxidation of its combustible elements (carbon and hydrogen in the present case) using its own oxygen [18]. An explosive substance is said to have a "high oxygen content" when

$$c - 2a - \frac{b}{2} \geqslant 0 \tag{3}$$

In such a case, the oxygen available internally is sufficient to induce a complete combustion of the compound.

However, an explosive substance is said to have a "low oxygen content", but to be "fully convertible into gases", when

$$a \ll c < 2a + \frac{b}{2} \tag{4}$$

This is the situation of the NC samples investigated in this study. Even in the absence of oxygen in the calorimetric bomb, it is still possible to induce the combustion of a cellulose dinitrate (eqn. 5) or a cellulose trinitrate (eqn. 6) as follows

$$C_{12}H_{16}O_{18}N_4(s) = 5CO_2(g) + 7CO(g) + 7H_2(g) + 1H_2O(g) + 2N_2(g) \tag{5}$$

$$C_{12}H_{14}O_{22}N_6(s) = 5CO_2(g) + 7CO(g) + 2H_2(g) + 5H_2O(g) + 3N_2(g) \tag{6}$$

Such balanced equations result from the internal combustion of NC in the presence of a totally inert gas, argon for example. Equations (5) and (6) do not take into account all the secondary reactions which can be expected from NC combustion. For example, Trenin [19] suggested a general formula involving the formation of methane in the calorimetric bomb, mainly at low temperatures. We will not take these secondary reactions into account in the following discussion.

Average heats of explosion

The high energies which are released through NC combustion can be explained by the fact that NC is constituted of combustive and combustible elements. By definition, a combustive element is a supporter of combustion: for example, highly electronegative elements, such as oxygen and fluorine, which will burn combustible elements easily and briskly with a significant heat release. A supporter of combustion may also be a compound, in which electronegative elements are weakly bonded chemically, that reacts briskly with any combustible compound [20]: such is the case for nitrogen dioxide and other nitrogen oxides, but not nitrogen monoxide.

According to these definitions, gaseous oxygen has a high combustion power while gaseous nitrogen is not a supporter of combustion. Therefore, any increase in the nitrate content of NC increases the combustive power of the sample towards its carbon skeleton which acts essentially as a combustible element.

When an excess of gaseous nitrogen is present in the calorimetric bomb, the normal internal combustion process of NC (in the absence of a reactive gas) is perturbed: there is a modification of the reaction stoichiometry, which favors an increased production of nitrogen oxides as secondary reaction products. The nitrogen oxides, formed through the action of nitrogen on the nitrocellulosic chain, modify the rupture process which would occur in the absence of the nitrogen atmosphere.

In fact, the combustion of a solid substance requires a rearrangement of the chains to permit the formation of volatile and stable species during reaction. When present, nitrogen monoxide hinders such rearrangements. However, in the presence of oxygen, radical nitrogen monoxide is converted into nitrogen dioxide, which favors primary rearrangements. Then, there is a competition between the inhibitory effect of nitrogen monoxide and the promoting effect of nitrogen dioxide upon the rearrangement of the chains [21]. This competition depends primarily on the following equilibrium

$$2NO^{\cdot} + O_2 \rightleftharpoons 2NO_2^{\cdot} \qquad (7)$$

In heat of explosion experiments, the absence of oxygen as a surrounding medium restricts this reaction. There is an excess of nitrogen monoxide which slows down the degradation of NC. This gives heats of explosion which are expected to be slightly lower than those measured following a regular internal combustion.

In order to test this hypothesis and to quantify the action of a nitrogen atmosphere on NC combustion, a sample of NCW-1342 was burned in a Parr calorimetric bomb under a totally inert atmosphere, the gas used being argon. Prior to this experiment, it was expected that the internal heat of combustion would be above the average heat of explosion, but below the average heat of combustion. The result obtained confirms this hypothesis: in a nitrogen atmosphere, the sample NCW-1342 has an average heat of explosion of 3.97 ± 0.07 kJ g^{-1}, whereas in an argon atmosphere, its internal heat of combustion is 4.36 ± 0.05 kJ g^{-1}. The difference between these two values is significant.

NC combustion under an argon atmosphere enabled us to determine the internal heat of combustion of the macromolecule without any modification of the degradation process coming from the surrounding medium. This method gives evidence of an inhibitory effect of the nitrogen gas on the internal heat of combustion of NC, as verified by the heat of explosion experiments.

On the other hand, in a nitrogen atmosphere, an increase in the nitrogen content of NC creates a slight increase in the average heat of explosion. This phenomenon will be discussed in the following section.

Average heats of combustion

We have previously shown (eqns. 5 and 6) that it is not necessary to add oxygen to the calorimetric bomb to ensure a total combustion of NC. Measurements carried out in an argon atmosphere enabled us to evaluate not only the internal heat of combustion of NC, but also the inhibitory effect of a gas such as nitrogen, or the combustive action of an oxygen atmosphere during combustion.

In the measurement of the heat of combustion of NC, two substances having a high combustive power are present: NC and oxygen. In an argon atmosphere, the internal heat of combustion for NCW-1342 is 4.36 ± 0.05 kJ g^{-1}. In an oxygen atmosphere, the average heat of combustion for the same sample increases to 9.52 ± 0.04 kJ g^{-1}. The contribution of oxygen to the combustion of NC is then obvious: the combustive action of gaseous oxygen is added to the internal combustion of NC through a series of energy exchange processes between the diatomic and radical species. Therefore, the average heat of combustion of NC is high, notwithstanding the various secondary reactions still possible in the system.

However, an increase in the nitrogen content of NC promotes the formation of gaseous nitrogen during combustion. The bond strength of $N\equiv N$ and the important energy gap which separates its highest occupied molecular orbital (HOMO) from its lowest unoccupied molecular orbital (LUMO) indicate that nitrogen is a relatively inert gas, short of any combustive power.

Since gaseous nitrogen is not a supporter of combustion, its presence inside the calorimetric bomb may slow down the combustion of NC. This phenomenon leads to a slight decrease of the average heats of combustion with increasing nitrogen content (Fig. 6).

On the other hand, the increase of the average heats of explosion with nitrogen content is due to the greater probability of forming nitrogen dioxide during the combustion of NC having a high nitrogen content. The role of oxygenated derivatives on the internal combustive power of NC is quite significant.

When NC burns in the presence of oxygen, the combustive power of the oxygen is so large that the action of oxygenated derivatives becomes negligible. Besides, fragmentation of nitrogen oxides involves the formation of nitrogen as a stable species which decreases the total energy of the system.

However, in a nitrogen atmosphere, supplementary traces of oxygen, coming from the nitrate groups on the chain, sufficiently increase the internal combustive power of NC so that the average heat of explosion of NC can increase slightly with increasing nitrogen content (Fig. 7).

The general behavior of the curves, for the average heats of explosion and combustion as a function of the nitrogen content of NC, shows once again the influence of the surrounding gaseous medium. The simultaneous presence of nitrogen and oxygen atoms along the nitrocellulosic chain creates a competition between the internal inhibitory effect, due to nitrogen formation, and the internal combustive action, corresponding to oxygen formation during combustion. In view of the results presented in this article, combustion of NC under a combustive atmosphere favors the internal inhibitory effect when the nitrogen content of NC increases. Under a non-combustive atmosphere, the internal inhibitory effect becomes less important compared to the combustive action of the internal oxygen which increases when the nitrogen content of NC increases.

Average heats of decomposition

The thermal decomposition of NC initially occurs through a rupture of the $RO-NO_2$ bonds [22–24]. This reaction creates radical species which control the secondary reactions during decomposition.

Studies by Wolfrom et al. [25,26] led to the identification of various by-products resulting from NC decomposition. Following the rupture of the $RO-NO_2$ bonds, secondary reactions permit the formation of volatile products such as CO, CO_2, NO, N_2O, NO_2, N_2, CH_4, H_2, HCHO and H_2O. The various nitrogen oxides formed originate from a rupture of the $RO-NO_2$ bonds. The presence of formaldehyde indicates that there is a breakage of the C_5-C_6 bond following the departure of nitrogen dioxide. The presence of the other substances can only be explained by assuming the rupture of several rings along the NC chain.

However, these ring-opening reactions are not complete since a residue is recovered at the end of the heat treatment, whereas no residue could be observed following heats of combustion and explosion measurements in the calorimetric bomb. The remaining residue represents 15–20% of the initial NC sample. The occurrence of such an important residue explains the obtention of small average heats of decomposition, of about 2.0 kJ g^{-1}. This proves that thermal decomposition leads to an incomplete combustion of NC since the heat of internal combustion, corresponding to the complete destruction of NC, is greater than 4.0 kJ g^{-1}.

Combustion of cellulosic materials relies upon two main reactions: flaming combustion and smoldering combustion. Flaming combustion implies a gas phase oxidation of the volatile products obtained through pyrolysis, while smoldering combustion involves a solid-phase oxidation of the remaining chars after the evaporation of all volatile products [27].

In the present study, pyrolysis of NC fibers occurs in a uninsulated DSC container submitted to a nitrogen current which carries out the volatile products that could have induced smoldering combustion of the remaining chars. Since smoldering combustion of NC does not take place to a significant extent, it is assumed that the residue from the thermal decomposition is primarily constituted of simple fragments from degraded and oxidized NC.

However, Eisenreich and Pfeil [28] have reported that the residue coming from the thermal degradation of a cotton NC contains more than 95% carbon. Therefore, most of the carbon–carbon bonds have been broken down, meaning that the probability of having oligomers or complex chains in the residue is small. A similar characterization was not made for NC derived from wood.

A thermogravimetric study carried out in our laboratory [29] proved that the physical aspect of the residue after thermal degradation is different for NC derived from wood and cotton: the NC derived from wood decomposes into a powdery residue while that derived from cotton gives a rather tarry residue. Additional work is being pursued in order to elucidate the specific relationship between residue formation and nitrocellulose origin.

CONCLUSIONS

Using the DSC method and the procedure described in this article, it is possible to measure average heats of decomposition of NC with a precision of the order of 2%.

Measurements were carried out for seven different samples, three derived from wood (NCW) and four derived from cotton (NCC), having a nitrogen content varying between 12.6 and 13.5%. It was observed that the average heat of decomposition of dried NC fibers increases slightly with nitrogen content, the values ranging between 1711 and 2050 J g^{-1}. The effect of various solvents (acetone, THF and ethyl acetate) on NC thermal decomposition was also demonstrated.

Average heat of combustion and explosion measurements of dried NC fibers were also made using bomb calorimetry. The values obtained are in the order of 4.0 and 9.5 kJ g^{-1} for the average heats of explosion and combustion, respectively. Results show a slight decrease of the average heats of combustion and a slight increase of the average heats of explosion with nitrogen content.

The measurement of the internal heat of combustion of NC, as determined in an argon atmosphere, demonstrated the combustive action of oxygen and the inhibitory effect of nitrogen towards NC degradation.

ACKNOWLEDGMENTS

This work was supported by the Department of Supplies and Services of Canada (Contract No. 85082-00150). All NC samples were supplied by the Defence Research Establishment of Valcartier. The authors thank J. Paquet and J.-J. Jutier for their experimental assistance and for fruitful discussions.

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