Thermochimica Acta, 27 (1978) 339–346
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE INFLUENCE OF COPPER AND LEAD COMPOUNDS ON THE THERMAL DECOMPOSITION OF NITROCELLULOSE IN SOLID PROPELLANTS

N. EISENREICH AND A. PFEIL
Fraunhofer-Gesellschaft, Institut für Chemie der Treib- und Explosivstoffe, D-7507 Pfinztal-Berghausen (Germany)

(Received 23 January 1978)

ABSTRACT

The thermal decomposition of pure nitrocellulose and nitrocellulose in double-base propellants containing Pb_3O_4, Cu(II) and Pb(II) salicylate as burning catalysts (modifiers) and the catalyst-free matrix were analyzed by TG and quantitative DTA (DSC). Parameters like rate constants, pre-exponential factors, activation energies and heats of reaction were determined where homogeneous kinetics could be assumed. The presence of modifiers manifests itself in lower activation energies, higher rate constants and higher heats of reaction at pressures below 30 bar. The results indicate that modifiers catalyze the thermal decomposition of nitrocellulose.

INTRODUCTION

The presence of catalysts (modifiers) alters the burning characteristics of double-base propellants in a distinct way. Though intensively studied[1-5], the underlying reaction mechanism is far from being understood.

The following study was undertaken to get new information on the mode of action of these modifiers using methods of thermal analysis such as TG and quantitative DTA (DSC). Of particular interest were (1) the determination of major steps of the thermal decomposition of double-base propellants and (2) the determination of kinetic parameters and the influence of modifiers on these parameters. Preliminary results in this regard were presented recently[6].

KINETICS

The DTA and TG curves were analyzed assuming the kinetics

$$\frac{dy}{dt} = -ky^n \tag{1}$$

where y is the concentration of the reactant, t the time, n the order of reaction and k

the rate constant. The concentration is related to quantities actually recorded by

$$-\frac{dy}{dt} \sim q(t) \sim \frac{dW}{dt} \tag{2}$$

where $q(t)$ designates the production of heat and dW/dt the weight loss.

If a linear heating rate α is applied, the term dt in eqn. (1) can be substituted by the temperature differential dT.

$$\frac{dy}{dT} = -\frac{1}{\alpha} k y^n \tag{3}$$

Based on the kinetics described above, the reaction parameters k, n, the activation energy E and the pre-exponential factor z can be calculated using the following expressions.

(a) Isothermal DTA and TG.

From a logarithmic and a double logarithmic plot of q or W versus t, the parameters n and k are determined. E and z are obtained by plotting the rate constants versus $1/T$ (Arrhenius plot).

$$\ln k(T) = \ln z - \frac{E}{RT} \tag{4}$$

(b) Method of Rogers and Morris[7].

The activation energy is obtained from a plot of $\ln q(T)$ versus $1/T$.

$$\ln q(T) \sim \frac{E}{RT} \tag{5}$$

Expression (5) holds only for the first part of the rising slope of the DTA curve.

(c) Method of Borchardt and Daniels[8].

$$\ln\left(-W^{-n}\frac{dW}{dT}\right) = \ln\frac{z}{\alpha} - \frac{E}{RT} \tag{6}$$

(d) Method of Kissinger[9].

$$\ln\frac{\alpha}{T_m^2} = \ln\frac{Rz}{E} - \frac{E}{RT_m} \tag{7}$$

where T_m is the peak temperature of the DTA curve.

Equations (4)–(7) allow an analysis of the experimental curves by linear regression. The kinetic parameters reported in this paper were obtained in this way with correlation coefficients better than 0.99 in all cases. The influence of modifiers on these parameters were elucidated by analysis of variance. Differences are stated with a confidence level of at least 95%.

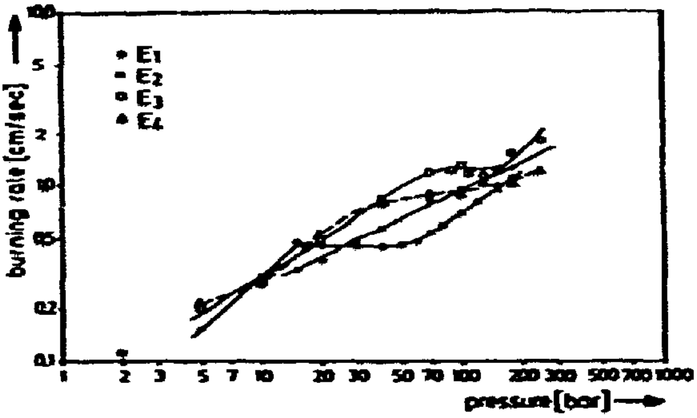

Fig. 1. The dependence of the burning rate on pressure measured by a Crawford type strand burner.

EXPERIMENTAL

The following samples were used: pure nitrocellulose (NC) containing 13.3% N, pure nitroglycerine (NG), a concentrate of 85% NG in 15% NC (NG/NC) and four double-base propellant compositions (E_1, E_2, E_3 and E_4).

The propellant E_1 (matrix) consisted of 51.5% NC, 34.5 NG/NC, 11% triacetin and 3% ethylcentralite I. E_2, E_3 and E_4 were modified propellants of the same matrix containing, in addition, 4% Pb_3O_4, Pb salicylate or Cu salicylate, respectively.

The propellants were characterized by their heat of explosion and their burning rate at different pressures. The heat of explosion in cal/g at 0.1 g/cm^3 loading density was 908 (E_1), 839 (E_2), 866 (E_3) and 851 (E_4). E_2 displayed a plateau at pressures between 15 and 45 bar, E_3 between 100 and 130 bar and E_4 between 40 and 180 bar. The variation of the burning rate with pressure is shown in Fig. 1 for E_1, E_2, E_3 and E_4. Samples of NC were prepared by casting films from mixtures of NC in acetone to which about 4% of the modifier was added.

A 990 Dupont Thermal Analyzer fitted with a quantitative DTA pressure cell was used for the experiments. Samples weighing between 1 and 3 mg were cut from the propellant strand and placed into capped aluminium pans. The lid was pierced several times to allow gaseous products to escape. The samples were analyzed in air or in a nitrogen atmosphere (99.995%) at pressures ranging from 0.01 to 60 bar. The heating rates were varied between 0.5 and 100 K/min. On the same instrument, isothermal quantitative DTA experiments were carried out in the 420–500 K temperature range. The samples were analyzed in air and heated to the desired temperature at a rate of 20 K/min. Simultaneous DTA and TG curves were recorded on a Mettler Thermoanalyzer in air with a purge rate of 10 l/h.

RESULTS AND DISCUSSION

Figure 2 shows TG curves of NC, NG/NC and E_1 at a heating rate of 0.5 K/min. Compared with NC and NG/NC, the weight loss of E_1 occurs in two distinct

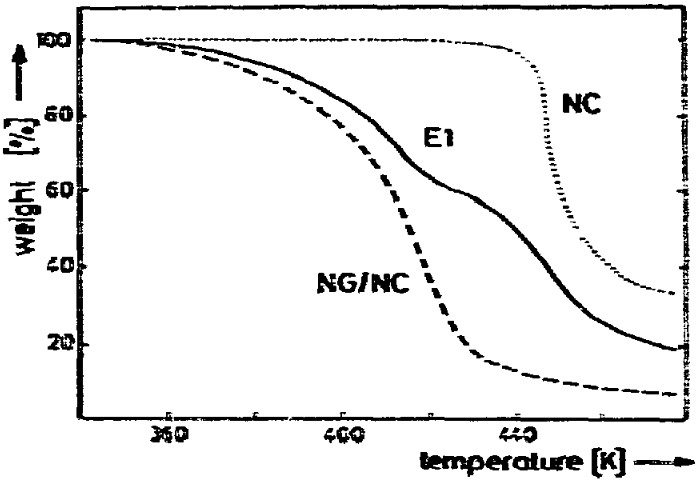

Fig. 2. Typical TG curves of a double-base propellant and components recorded at a heating rate of 0.5 K/min.

steps caused by the evaporation of NG up to 420 K and the subsequent decomposition of NC up to 470 K. During the decomposition, a residue was formed in the amount of about 20% of the initial weight which disappeared at temperatures above 600 K.

The first step is endothermic as exhibited by the DTA curve which was recorded simultaneously. The weight loss corresponds to the amount of NG present in E_1. The activation energy of this step is 13.8 kcal/mole and agrees well with those of pure NG, NG/NC, E_2, E_3, E_4 and the heat of evaporation of pure NG obtained from vapour pressure data[10-12]. A similar value was found by Alexandrov and Klevnoi[13] for the diffusion-controlled evaporation of NG in propellants.

The second step in the TG curve is related to the exothermic decomposition of NC. The activation energy for E_1 is 45.3 kcal/mole as calculated from the TGA curve at a 0.5 K/min heating rate. The corresponding energies of the modified propellants are lower, 39.3 kcal/mole, 39.1 kcal/mole and 32.0 kcal/mole, respectively, for E_2, E_3 and E_4. The activation energies of the two steps were calculated from eqn. (6) assuming $n = 1$. The corresponding pre-exponential factors are 7.7×10^{18}, 5.6×10^{15}, 2.3×10^{16} and 3.5×10^{12} sec^{-1} for E_1, E_2, E_3 and E_4, respectively. At higher heating rates, the two steps in the thermal decomposition of the propellants were less clearly separated and it was not possible to obtain reliable data for the calculation of activation energies from the TG experiment. In the quantitative DTA experiments at heating rates up to 100 K/min, the exothermic step only was observed. From a comparison with the TG curves, this step was attributed to the exothermic decomposition of NC.

Figure 3 depicts the rate constants at different temperatures calculated from isothermal DTA curves. Whereas the activation energies calculated from eqn. (4) do not reflect clearly an influence by the modifiers, the rate constants, in contrast, do. They are significantly higher for E_2 and E_3 with respect to the unmodified E_1. The reaction was found to be of first order which is generally accepted for the thermal decomposition of NC in the presence of stabilizers like ethylcentralite[14].

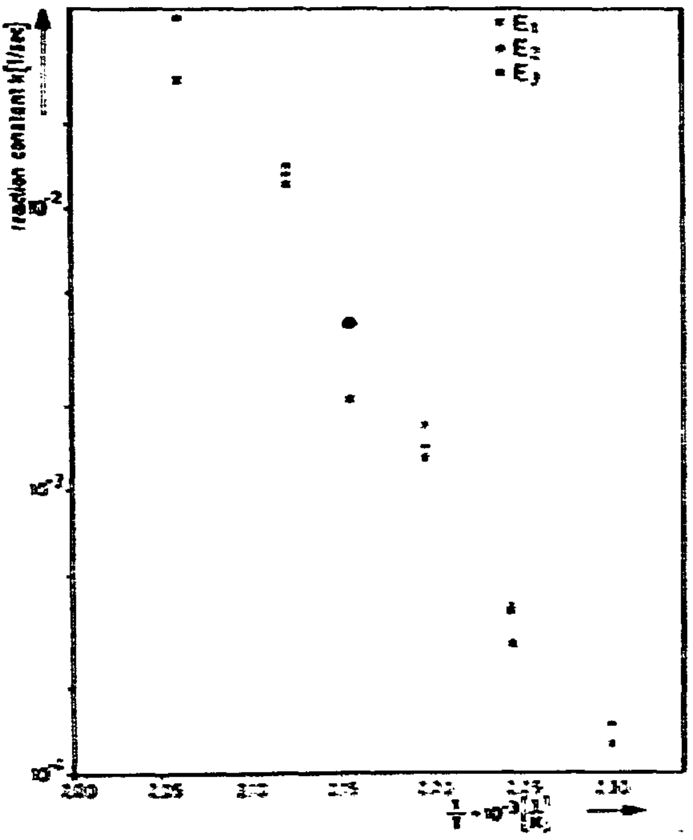

Fig. 3. Arrhenius plot of the rate constants calculated from isothermal quantitative DTA.

The initial slope of quantitative DTA curves at pressures between 0.01 and 60 bar and heating rates ranging from 0.5 to 100 K/min were analyzed using the method of Rogers and Morris. This method is represented by eqn. (5). A typical result at 1 bar and a heating rate of 0.5 K/min is shown in Fig. 4. The graph demonstrates the difficulty encountered in many cases that small shoulders on the rising slope prevented a thorough analysis. The same observations were also made by Kirby and Suh in their DTA study of unmodified propellants[15]. However, activation energies were calculated and good correlation coefficients were obtained in all cases where the difficulties were less.

The values of the energies obtained in this way differ considerably and range from 30 to 50 kcal/mole. No definite trend with pressure, heating rate or added modifier was evident. Since the sample is highly exothermic and hence only a small amount (1–3 mg) could be analyzed during a quantitative DTA run, the large range reflects the inhomogeneity of the propellants used. Also, the values cited in the literature for the decomposition of pure NC and of NC mixed with different additives like plasticizers, stabilizers or mixtures thereof range from 30 to 50 kcal/mole[13, 14, 16–18].

Using the plot according to Rogers and Morris, the activity of the modifiers is nevertheless visible if one compares the production of heat at the initial slopes of the

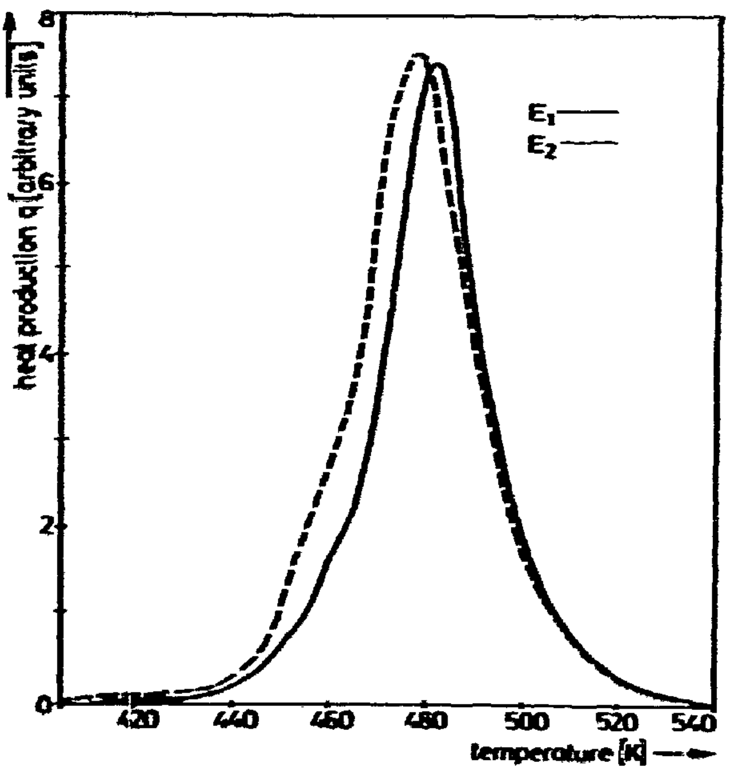

Fig. 4. Typical DTA curves of the propellants E$_1$ and E$_2$ recorded at a heating rate of 20 K/min.

DTA curves. Since the same amount of sample was always used in this experiment, the graphs can be compared directly showing clearly that q of E$_2$ and E$_3$ is higher with respect to E$_1$. This corresponds to the result already discussed in the isothermal quantitative DTA studies that the rate constants of the modified propellants are higher than that of the unmodified.

Kinetic parameters according to eqn. (7) (Kissinger's method) were obtained from an analysis of the peak temperatures, T_m. They were determined from quantitative DTA curves at 1 bar in air and at heating rates between 0.5 and 100 K/min. T_m was found to be always lower for the modified propellants compared with the unmodified. An analysis of the data by linear regression resulted in activation energies of 35.6, 31.8, 32.7 and 33.2 kcal/mole for E$_1$, E$_2$, E$_3$ and E$_4$, respectively. The corresponding pre-exponential factors are 2×10^{14}, 5.1×10^{12}, 1.4×10^{13} and 2.3×10^{13} sec^{-1}. As already found from the analysis of the TG curves, the activation energies of E$_2$, E$_3$ and E$_4$ are smaller than that of E$_1$.

The heats of reaction, obtained by integrating the quantitative DTA curves, of E$_1$, E$_2$ and E$_3$ at different pressures and a heating rate of 20 K/min are depicted in Fig. 5. The data presented are mean values of about 4 measurements. They were analyzed on the basis of a two way analysis of variance with respect to sample and pressure. With a confidence better than 95%, it can be stated that the heat of reaction is dependent on pressure in the range below 30 bar and that the modified samples have the higher heats of reaction in this range. The same results were obtained for E$_4$.

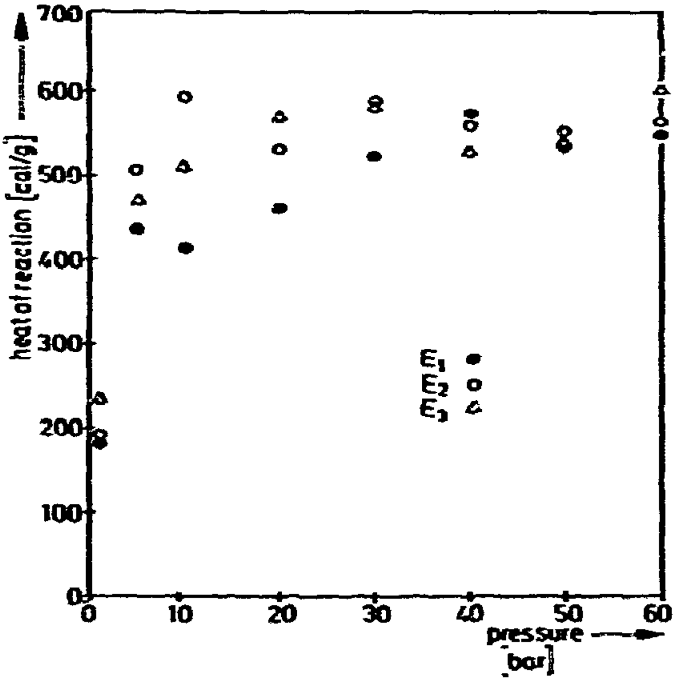

Fig. 5. Heat of reaction at different pressures (N_2 atmosphere) measured at a heating rate of 20 K/min.

A similar dependence on pressure was reported for the heat of explosion of comparable propellants[5].

Since the lids of sample pans were pierced to allow an easy escape of the gaseous products, contributions by gaseous reactions to the measured heats are expected to be minor at lower pressures (below 30 bar). This implies that the modifiers predominantly catalyse condensed phase and/or heterogeneous reactions in this pressure range, that is, as shown in the discussion of the TG and DTA curves, the thermal decomposition of NC in the propellant.

Of particular interest, therefore, was the observation of the catalytic effect on pure NC. A typical result is shown in Fig. 6. The influence of the modifier manifests itself in the shift of the quantitative DTA curve to lower temperatures. This effect, however, was not observed from samples which were prepared by simple mechanical mixing of the components. This observation indicates that a structural interaction of the catalyst with the NC is required for the catalytic effect to arise. Such an interaction was postulated by Suh et al.[2]. In the propellant, this interaction is obviously brought about by the rolling procedure during the manufacturing process.

A similar evaluation of kinetic parameters was not possible for pure NC since it does not decompose according to homogeneous kinetics. Manelis et al. described the thermal decomposition of pure NC as an autocatalytic reaction consisting of a primary and secondary reaction[18]. The shift of the DTA curve to lower temperatures indicates, however, that the primary rate constant of this process is increased under

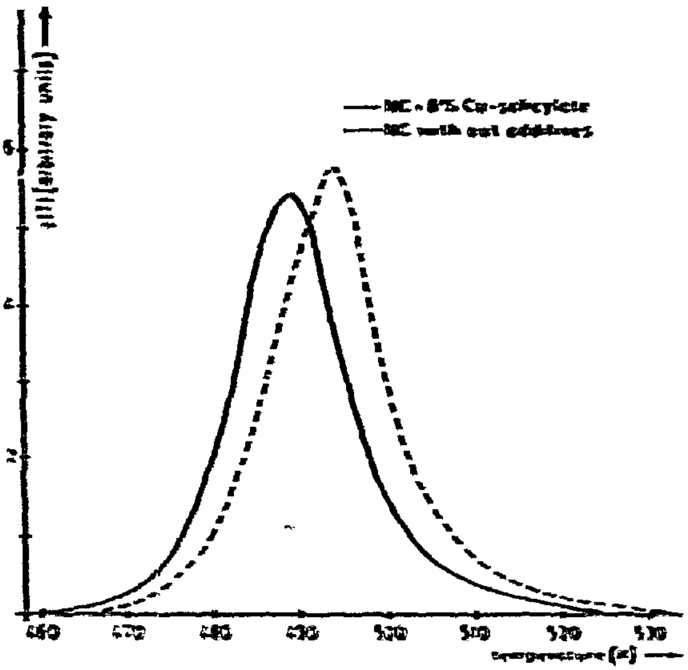

Fig. 6. Typical DTA curves of pure NC and a mixture of NC with 50% Cu salicylate at a heating rate of 20 K/min.

the influence of the modifier. In the propellants, the secondary reaction is suppressed by the presence of stabilizers allowing the evaluation of the data on the basis of simple kinetics.

REFERENCES

1 D. J. Hewkin, J. A. Hicks, J. Powling and J. Watts, *Combust. Sci. Technol.*, 2 (1971) 307.
2 N. P. Suh, G. F. Adams and C. Lenchitz, *Combust. Flame*, 22 (1974) 289.
3 N. Kubota, T. J. Ohlemiller, L. H. Caveny and M. Summerfield, *AIAA J.*, 12 (1974) 1709; *AMS Rep. 1087*, Princeton University, March 1973.
4 R. A. Fifer and J. A. Lannon, *Combust. Flame*, 24 (1975) 369.
5 C. Lenchitz and B. Haywood, *Combust. Flame*, 10 (1966) 140.
6 N. Eisenreich and A. Pfeil, *First European Symposium on Thermal Analysis, Salford, U.K.*, 1976.
7 R. N. Rogers and E. D. Morris, *Anal. Chem.*, 39 (1966) 412.
8 H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, 79 (1957) 41.
9 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
10 A. Marshall, *J. Soc. Chem. Ind.*, 23 (1904) 128.
11 W. de C. Crater, *Ind. Eng. Chem.*, 21 (1929) 674.
12 A. Marshall and G. Peace, *J. Soc. Chem. Ind.*, 109 (1916) 298.
13 V. V. Alexandrov and S. S. Klevnoi, *Fiz. Goreniya Vzryva*, 4 (1970) 435.
14 R. W. Philips, C. A. Orlich and R. Steinberger, *J. Phys. Chem.*, 59 (1955) 1034.
15 C. E. Kirby and N. P. Suh, *AIAA J.*, 9 (1971) 317.
16 A. G. Mershanov, *Combust. Flame*, 11 (1967) 201.
17 V. V. Alexandrov and N. S. Bufetov, *Fiz. Goreniya Vzryva*, 7 (1971) 306.
18 G. B. Manelis, Yu. I. Rubtsov, L. P. Smirnov and F. I. Dubovitsky, *Kinet. Katal.*, 3 (1962) 42.