Thermochimica Acta, 29 (1979) 305–308

A THERMOANALYTICAL STUDY OF THE CATALYTIC OXIDATION OF CARBONACEOUS RESIDUES OF NITROCELLULOSE DECOMPOSITION

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ABSTRACT

Carbonaceous residues of nitrocellulose and doublebase propellants were collected from TA and combustion experiments and analyzed in air by TG and quantitative DTA.

The residues react like charcoal. Burning catalysts like lead and copper salicylates have a strong influence on the reaction interval and kinetic parameters.

INTRODUCTION

Under certain conditions pure NC[*] and NC contained in DB thermally decompose under formation of a carbonaceous residue. This residue, for example, is observed during slow heating of NC or DB in a TA experiment or during combustion of DB in a bomb.

The oxidation process of this material is an important step in the combustion of DB (refs. 1-2). In this paper, the oxidation reaction of the carbonaceous material in air and the influence of burning catalysts is studied.

METHODS

The following samples were analyzed by simultaneous TG/DTA (Mettler Thermoanalyzer, sample weight 5 mg, heating rate 1 K/min) and quantitative DTA (Dupont 990 Thermoanalyzer, sample weight 0.5 - 1.0 mg, heating rate 10 K/min) in air (purge rate 10 l/h):

1) Carbonaceous residues of DB combustion in a Crawford type strand burner. The DB samples were E1 (catalyst-free), E2 (4% Pb_3O_4), E3 (4% Pb salicylate) and E4 (4% Cu salicylate) (details see ref. 3).
2) Carbonaceous residues of E1, E2, E3 and E4 obtained after heating to 523 K at a rate of 1 K/min in air.

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[*] Abbreviations used: DB = doublebase propellant, NC = nitrocellulose

3) Carbonaceous residues of NC (13.3% N) obtained after heating to 523 K at a rate of 0.5 K/min in air and mixtures of the residue with 4% Cu salicylate or 4% Pb salicylate.
4) Charcoal and activated charcoal (Merck), charcoal of black peat, white peat and beech (Dynamit Nobel AG) and their mixtures with 4% CuO, Pb_3O_4, Cu salicylate or Pb salicylate.

Assuming simple reaction kinetics, activation energies E and pre-exponential factors z were calculated from a direct least squares fit of the TG and quantitative DTA curves using E and z as fit parameters (ref. 4). The following fitting curve was used:

$$y(T) = \exp\left[-z/\alpha \int \exp(-E/RT)\, dT\right] \qquad (1)$$

(y denotes the sample weight, T the temperature, α the linear heating rate and R the universal gas constant).

The quantitative DTA curves normalized on the area were fitted by the first derivative of (1).

RESULTS

Fig. 1 shows typical thermal diagrams of the DB samples. The DTA curves display a strong exothermic peak at temperatures above 600 K, in addition to those described in ref. 3. In the presence of burning catalysts the reaction interval is shifted drastically to lower temperatures.

Similar observations were made in the thermal diagrams of the combustion residues of the DB samles, the residues of the slow thermal decomposition of NC and the carbon samples (e.g. Figs. 3-4).

An analysis of the carbonaceous residues yielded a carbon content of $\geqslant$95%. The IR spectra in Fig. 3 show that the characteristic C-H and N-O bands of NC (I) and the C-O band of pre-heated NC (II) are absent in the residues of NC (III) and DB combustion (IV).

TABLE 1

Kinetic parameters of the oxidation reaction

sample	E	log z	%	sample	E	log z	%
	kcal/mole				kcal/mole		
combust.res. E1	27.0	5.99	2.5	NC pure	29.8	5.92	0.8
E2	23.0	5.33	2.6	+ Cu sal	21.1	3.51	0.8
E3	not evaluated			+ Pb sal	45.6	11.54	1.3
E4	22.0	5.67	2.9	charcoal	28.4	5.59	0.7
decomp.res. E1	27.5	4.89	0.9	+ Cu sal	28.9	6.00	1.3
E2	86.0	24.85	1.3	+ CuO	26.2	4.99	1.0
E3	60.5	15.85	0.9	+ Pb sal	34.0	7.99	0.8
E4	24.2	5.20	0.6	+ Pb_3O_4	30.2	6.78	0.8

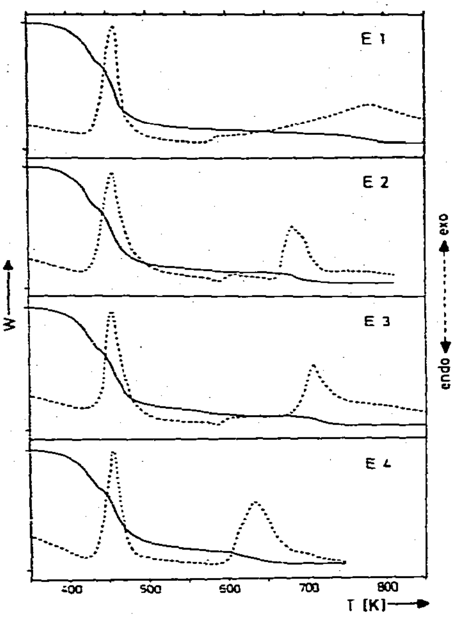

Fig. 1. TG / DTA of DB samples at a heating rate of 2 K/min.

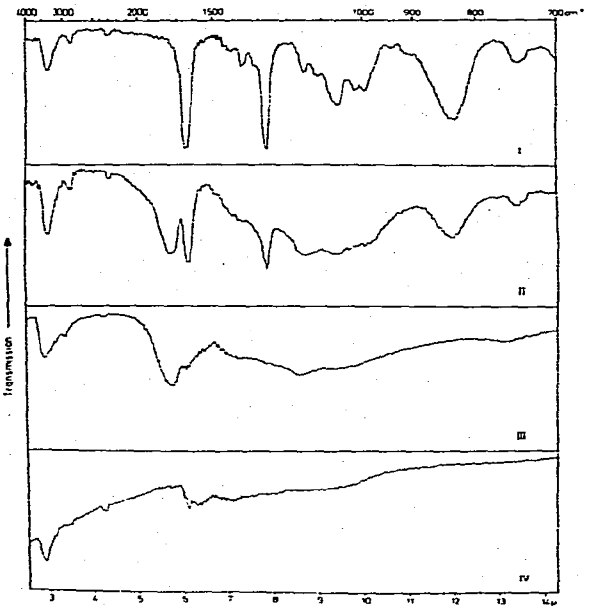

Fig. 2. IR spectra of NC (I), thermally pretreated NC (II, III) and E2 combustion residue (IV).

In Figs. 3-4 experimental quantitative DTA and TG curves represented by a series of points are compared to the corresponding fit curves which were calculated assuming simple first order kinetics. The parameters are summarized in Table 1. The quality of the fit is expressed by the mean standard deviation which is ≤ 1 in most cases. The mean standard deviation of the second order fit curves were significantly higher in all cases.

The parameters of charcoal were closest to those obtained for the combustion and thermal decomposition residues of DB and NC. The activation energies for activated charcoal and the charcoals of white peat, black peat and beech were 46.8, 38.6, 41.1 and 45.6 kcal, respectively. A linear relationship was found between the parameters of all samples in a plot of log z against E.

DISCUSSION

In view of the small standard deviation we used simple first order kinetics to describe the experimental results. The kinetic parameters in Table 1 suggest that, under the conditions stated, NC or NC in DB thermally decompose into a charcoal type material. The oxidation process of this material is like that of charcoal.

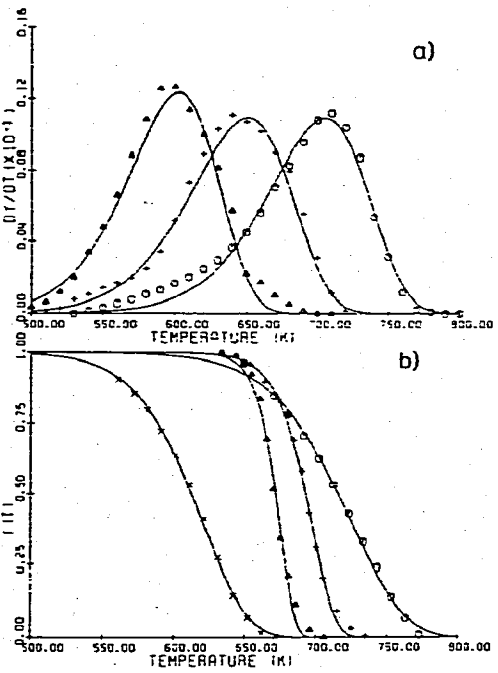

Fig. 3. DTA of combustion residues E1 (O), E2 (+) and E4 (▲) at a heating rate of 10 K/min (a) and TG of decomposition residues E1 (O), E2 (▲), E3 (+) and E4 (x) at a heating rate of 1 K/min (b).

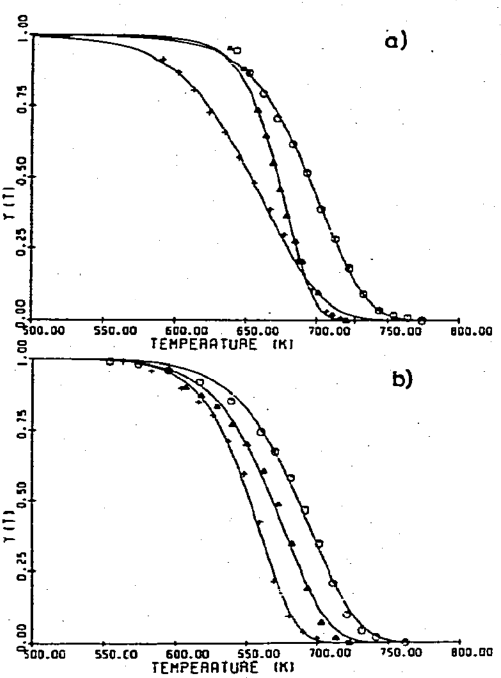

Fig. 4. TG of decomposition residues NC (O), NC + Cu sal (+) and NC + Pb sal (▲) at a heating rate of 1 K/min (a) and TG of charcoal (O) with Cu sal (▲) and Pb sal (+) at a heating rate of 1 K/min (b).

The IR spectra reflect characteristic steps in the formation of the charcoal type material during the thermal decomposition of NC by the change or disappearance of C-H, C-O or N-O bands. The activation energies of the oxidation reaction of charcoal and the catalyst-free NC and DB residues are comparable and agree well with those reported in the literature (ref.5).

The burning catalysts have a drastic influence on the oxidation process of all samples studied. In DB compounds the burning catalysts act in two ways: they catalyse the decomposition of NC (ref. 3) and are still active during the oxidation of the charcoal type residue formed during decomposition.

ACKNOWLEDGEMENT

We are indebted to Texdata Vertriebs-GmbH, Ettlingen for writing our draft on their VYDEC word processing system.

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