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THERMAL DECOMPOSITION KINETICS

PART IX. A STUDY OF THE THERMAL DECOMPOSITION OF SODIUM TETRAPHENYL BORATE*

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ABSTRACT

Sodium tetraphenylborate [$NaB(C_6H_5)_4$] undergoes a two-stage decomposition on heating in air. The DTG peak temperatures are at about 320 and 500°C, the corresponding DTA peaks are at 330 and 520°C. The energies of activation for the two stages are ≈ 220 kJ mol^{-1} and ≈ 140 kJ mol^{-1}. The total enthalpy change for the complete decomposition (including combustion of carbonaceous decomposition products) is $\approx -13{,}200$ kJ mol^{-1}. The ultimate decomposition product in air is $NaBO_2$.

INTRODUCTION

Some tetracovalent boron compounds have recently attracted the attention of propellant technologists by virtue of their influence on the burning rate of perchlorate-based composite propellants[1,2]. While a considerable amount of work has been done on the thermal decomposition of perchlorates, comparatively much less attention has been paid to the thermal behaviour of tetracovalent boron compounds. This prompted us to start a programme of investigation of the thermal decomposition of some typical boron compounds.

Wendlandt and co-workers[3] have made an early thermogravimetric study of tetraphenylborates of some alkali metals. According to their published TG curves, the decomposition generally starts at ≈ 250°C and reaches a maximum at ≈ 320°C. Korenman and Sidorenko[4] observed that no loss of boron occurred on calcination of sodium tetraphenylborate. Our results are in agreement with these earlier observations. A search through the literature did not reveal any earlier study of the kinetic parameters of the decomposition. In this communication we wish to present the results of our studies on the kinetics of thermal decomposition of sodium tetraphenylborate.

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EXPERIMENTAL

Sample

Sodium tetraphenylborate [$NaB(C_6H_5)_4$] (E. Merck, W. Germany) was used as such. The guaranteed purity of the sample was 99.5%. The fraction between −140 and +200 B.S.S. was used.

Apparatus

Simultaneous TG–DTA curves were obtained on a Stanton thermobalance model TR-01 of 0.1 mg sensitivity. The samples were taken in standard dimpled platinum crucibles (8 mm × 6.2 mm diam.). The heating rate was 4°C $\min^{-1}$, chart speed 12 in. h^{-1} and the atmosphere was static air. The sample temperature was measured directly by means of a Pt–Pt/Rh thermocouple, the bead of which was positioned in the cavity of the crucible. The furnace temperature was recorded on the same chart as the TG curve.

In addition to the simultaneous TG–DTA in air, a separate DTA study was made in a nitrogen atmosphere. For this study, a Fisher DTA apparatus Model 260 F with linear temperature programmer Model 360 was employed. The heating rate was 5°C $\min^{-1}$. (A 4°C $\min^{-1}$ heating rate was not feasible with this instrument; therefore, the nearest available heating rate, viz., 5°C $\min^{-1}$ was used). The sample temperature was measured with a platinel thermocouple positioned directly in the sample taken in a quartz crucible.

Computational work was done on a Minsk II Computer, using the Algol programme.

Procedure

The samples were packed in the crucible in as identical a manner as possible and an equal quantity of calcined alumina was taken in the reference crucible. For simultaneous TG–DTA, three different sample masses were used (20, 30 and 40 mg) and duplicate runs were taken for each set to evaluate the reproducibility. For the separate DTA study in nitrogen employing the Fisher DTA equipment, a gas flow-rate of 50 cm^3 $\min^{-1}$ was used; 40 mg samples were used here.

Independent pyrolysis studies were carried out in open platinum crucibles. Quantitative analyses of the residues were done using standard analytical procedures.

Treatment of data

The instrumental curves were redrawn to obtain TG, DTG and DTA curves. The peak temperatures and the peak-base widths in DTG and DTA were noted. Enthalpy changes (ΔH values) were obtained from DTA curves by comparison with reactions with known enthalpy changes, carried out under identical conditions on the same DTA equipment.

Choice of a suitable kinetic equation

Four different kinetic equations were employed, viz., (1) Coats–Redfern; (2) MacCallum–Tanner; (3) Van Krevelen; and (4) Horowitz–Metzger equations. The former two represent "Integral methods" and the latter two "Approximation methods". The forms of these equations are given below where a term g(α) has been introduced for convenience and is defined as:

$$g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}$$

(1) Coats–Redfern[5]

$$\ln \frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{\phi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

(2) MacCallum–Tanner[6]. This equation is used in a modified form, retaining the form of R.H.S., but using the form of g(α) given here in the L.H.S.

$$\log_{10} g(\alpha) = \log_{10} \frac{AE}{\phi R} - 0.48E^{0.44} - \frac{(0.449+0.217E)\times 10^3}{T}$$

(3) Van Krevelen[7]

$$\ln g(\alpha) = \ln\left[\frac{A}{\phi}\left(\frac{e^{-1}}{T_s}\right)^{E/RT_s} \bigg/ \left(\frac{E}{RT_s}+1\right)\right] + \left(\frac{E}{RT_s}+1\right)\ln T$$

(4) Horowitz–Metzger[8]

$$\ln g(\alpha) = \ln\left(\frac{ART_s^2}{\phi E}\right) - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2}$$

[α = fraction decomposed; n = order parameter; T = temperature (K), A = pre-exponential factor; ϕ = heating rate in deg. sec^{-1}; E = energy of activation; R = gas constant; T_s = DTG peak temperature and $\theta = T - T_s$].

Determination of the order parameter 'n'

The computation method was employed for calculating 'n'. This method is based on the assumption that, that value of 'n' which gives the best linear fit for a particular kinetic equation (here, the Coats–Redfern equation was chosen for this purpose) should be the most acceptable value. The value of 'n' was thus varied from 0.05 to 2.15 in increments of 0.1, and using the computer, the linearity of the plot of $\ln g(\alpha)/T^2$ versus $1/T$ was tested for a 30 mg result set. The value which gave the best fit was accepted.

Evaluation of the energy of activation

After evaluating n, each of the kinetic equations (1–4) was employed to evaluate the energy of activation (E). The computational method was used for drawing the linear plots by the method of least squares and the correlation coefficient was calculated in each case.

RESULTS AND DISCUSSION

A typical set of TG, DTG and DTA curves in air and a DTA curve in nitrogen are given in Fig. 1. Table 1 gives the temperature range, peak temperatures, peak-base widths and the values of percentage loss in mass in TG–DTG experiments for the different sample masses (20, 30 and 40 mg). Similar data for DTA experiments in air and nitrogen are presented in Table 2 which also includes ΔH data. Mass-loss data for independent pyrolysis studies are given in Table 3.

The degradation of $NaB(C_6H_5)_4$ takes place in two stages. The first stage begins at around 260°C and is finished by about 400°C. The DTG peak temperature is in the range of 320–330°C. The second stage begins at around 400°C and is over by about 600°C; the peak is at about 500–540°C. The decomposition temperature ranges in DTA are close to those in TG for both stages. The first stage peak is strong and sharp in both DTG and DTA. The second stage in DTA is a medium and spread-out peak with a shoulder at around 470°C, while the corresponding DTG peak is very weak and blunt. It is also seen that whereas the inception temperature is not much

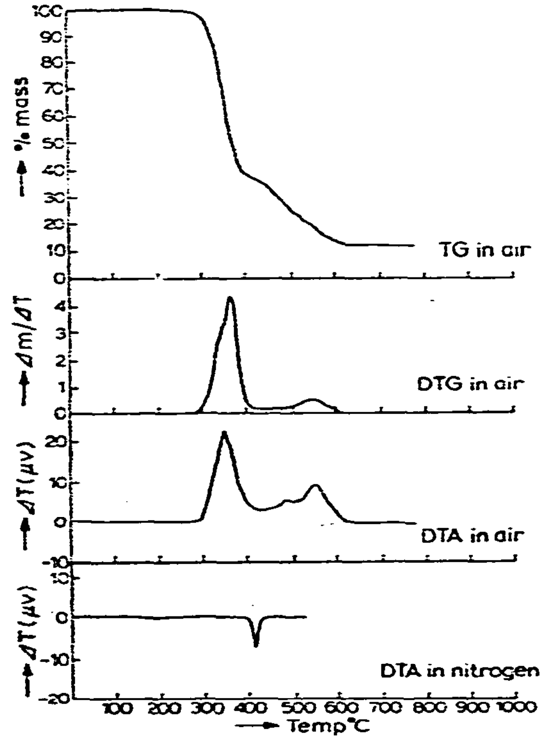

Fig. 1. Thermal decomposition curves of sodium tetraphenylborate.

TABLE 1

TG AND DTG RESULTS

Amount taken (mg)	*Run No.*	*First stage*				*Second stage*			*% Total mass loss*
		DTG peak temp. (°C)	*Peak-base width (°C)*	*Type of DTG peak*	*% mass loss*	*DTG peak temp. (°C)*	*Peak-base width (°C)*	*Type of DTG peak*	
20	1	323	260–400	Very strong and sharp	57.5	520	400–590	Very weak and blunt	85.0
	2	322	260–400	— do —	60.5	497	400–610	— do —	85.5
30	1	328	260–400	— do —	62.8	520	400–620	— do —	80.4
	2	332	270–400	— do —	61.0	525	400–600	— do —	82.7
40	1	333	270–400	— do —	65.3	543	400–600	— do —	85.7
	2	322	270–400	— do —	67.0	540	400–600	— do —	83.1

TABLE 2

DTA RESULTS

Amount taken (mg)	*Run No.*	*First stage*			*Second stage*			*Total reaction*
		DTA peak temp. (°C)	*Peakbase width (°C)*	*Peak type*	*DTA peak temp. (°C)*	*Peak-base width (°C)*	*Peak type*	*ΔH (kJ mol^{-1})*
In air								
20	1	330	282–376	Exothermic, sharp and strong	520	400–600	Exothermic, medium and spread shoulder at 460°C	−12,800
	2	330	174–370	— do —	530	440–600	— do — shoulder at 468°C	−13,600
30	1	355	265–381	— do —	505	445–610	— do — shoulder at 480°C	−12,700
	2	326	264–350	— do —	522	430–590	— do — shoulder at 470°C	−13,200
40	1	330	275–361	— do —	567	443–596	— do — shoulder at 476°C	−10,700
	2	324	241–380	— do —	570	443–602	— do — shoulder at 470°C	−11,900
In nitrogen								
40		432	420–440	Endothermic, sharp		NIL		+72

TABLE 3

DATA FROM INDEPENDENT PYROLYSIS STUDIES

Expt. No.	*First stage*		*Total reaction*		
	% mass loss	*Probable residue*	*% mass loss*	*Probable residue*	*% mass loss theor.*[a]
1	58.05	Not postulated; a tarry product is obtained	81.46	$NaBO_2$	81.30
2	60.26		81.52	$NaBO_2$	81.30
3	58.60		81.53	$NaBO_2$	81.30

[a] Calculated for the conversion of $NaB(C_6H_5)_4$ (containing 0.5% volatile matter at 105°C) to $NaBO_2$.

affected, the peak temperature increases slightly with the sample size. This is in agreement with the observations of earlier workers[9].

In view of the narrow nature of the stability plateau between the end of the first stage and the beginning of the second stage, it was not considered worthwhile to attempt product identification at this stage. The total mass loss at the end of the second stage (81.5%) is very close to the theoretical mass loss, calculated for the conversion of $NaB(C_6H_5)_4$ to $NaBO_2$. The quantitative analysis of the residue gives 35.3% Na and 13.6% B in comparison to 35.0% Na and 16.4% B for $NaBO_2$.

The first stage of the pyrolysis is $NaB(C_6H_5)_4 \rightarrow$ charred product + volatile organic materials. These volatile products are oxidised by air to give the first sharp exothermic peak in the DTA, and the second peak is due to the burning of the charred product in air. When the DTA was done in nitrogen atmosphere the exothermic peaks were absent, instead an endothermic change was observed at 420–440°C with a peak at 432°C and a black tarry residue was obtained.

The computational method gave $n = 1.15$ for the first stage and $n = 1.35$ for the second stage. With these values of 'n' the activation energy and the corresponding correlation coefficient, r, for both stages were calculated using the four equations, and the results are given in Tables 4 and 5.

The activation energy of the first stage is about 180–230 kJ mol^{-1} and that of the second stage is about 110–150 kJ mol^{-1} for different sample masses and equations. The correlation coefficients are very near to unity in all cases, indicating a near-perfect fit. There is a general decrease in E with increase in sample mass. This trend is also in agreement with the observations of previous workers[9].

The enthalpy change data may now be examined. It may be seen from Table 2 that the ΔH value for the whole decomposition process in air comes to about $-13{,}200$ kJ mol^{-1}. These very high values are explicable because they include the heats of combustion of the carbonaceous decomposition products. (The ΔH values obtained for larger sample masses, especially 40 mg samples, are lower, probably because the sample level here is much above the cavity containing the thermocouple). The ΔH value for the decomposition in nitrogen atmosphere is about $+72$ kJ mol^{-1}.

TABLE 4

ACTIVATION ENERGY AND CORRELATION COEFFICIENT FOR FIRST STAGE DECOMPOSITION ($n = 1.15$)

Sample mass (mg)	*Equation used*	*First experiment*		*Duplicate*	
		E(kJ mol^{-1})	*r*	*E(kJ mol^{-1})*	*r*
20	Coats–Redfern	224	0.982	216	0.984
	MacCallum–Tanner	227	0.984	219	0.985
	Van Krevelen	227	0.982	220	0.984
	Horowitz–Metzger	230	0.980	223	0.982
30	Coats–Redfern	202	0.999	197	0.999
	Mac Callum–Tanner	205	0.999	200	0.999
	Van Krevelen	208	0.999	206	0.999
	Horowitz–Metzger	214	0.999	214	0.999
40	Coats–Redfern	184	0.962	199	0.981
	MacCallum–Tanner	187	0.966	202	0.983
	Van Krevelen	186	0.963	203	0.981
	Horowitz–Metzger	189	0.959	221	0.990

TABLE 5

ACTIVATION ENERGY AND CORRELATION COEFFICIENT FOR SECOND STAGE DECOMPOSITION ($n = 1.35$)

Sample mass (mg)	*Equation used*	*First experiment*		*Duplicate*	
		E(kJ mol^{-1})	*r*	*E(kJ mol^{-1})*	*r*
20	Coats–Redfern	138	0.999	138	0.996
	MacCallum–Tanner	144	0.999	143	0.996
	Van Krevelen	148	0.999	146	0.998
	Horowitz–Metzger	158	0.999	155	0.999
30	Coats–Redfern	114	0.998	110	0.999
	MacCallum–Tanner	119	0.998	115	0.999
	Van Krevelen	124	0.998	119	0.999
	Horowitz–Metzger	134	0.996	127	0.997
40	Coats–Redfern	112	0.993	131	0.994
	MacCallum–Tanner	117	0.994	137	0.995
	Van Krevelen	122	0.992	142	0.995
	Horowitz–Metzger	133	0.988	153	0.995

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