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DECOMPOSITION OF CYCLOHEXYL-*t*-BUTYL-DIMETHYLAMMONIUM TETRAPHENYLBORATE
Synthesis and kinetics

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Abstract

A new compound cyclohexyl-*t*-butyldimethylammonium tetraphenylborate, $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4$ has been prepared, and its decomposition mechanism was studied by TG. The IR spectra of the products of thermal decomposition were examined at every stage. Kinetic analysis for the first stage of thermal decomposition process was obtained by TG and DTG curves, and kinetic parameters were obtained from the analysis of the TG-DTG curves with integral and differential equations. The most probable kinetic function was suggested by comparison of kinetic parameters.

Keywords: non-isothermal kinetics, quaternary ammonium, tetraphenylborate, thermal decomposition

Introduction

Sodium tetraphenylborate is widely used in inorganic analysis, organic analysis, modern electrochemical analysis, optical analysis, organic synthesis, catalysis etc. Since Witting and his coworker synthesized $NaBPh_4$ in 195 [1], the characteristics of alkali metal and alkaline earth metal tetraphenylborates have been widely studied. However, very little work is found in literature concerning ammonium and substituted ammonium compounds of tetraphenylborates, especially no work in respect of quaternary ammonium compounds. Here, one quaternary ammonium tetraphenylborate was prepared and characterized. The thermal decomposition mechanism and kinetic parameters were studied under non-isothermal conditions, the Achar differential equation [2] and the Coats-Redfern integral equation [3] were used to analyze

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the non-isothermal decomposition process. The integral and differential equations are as follows:

$$\ln(g(\alpha)/T^2) = \ln(AR/\beta E) - E/RT \quad (1)$$

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/RT \quad (2)$$

In the above equations, α – is the fractional decomposition, T – the absolute temperature (K), $d\alpha/dt$ – the reaction rate, A – the preexponential Arrhenius factor (S^{-1}), β – the heating rate (K min^{-1}), E – the apparent activation energy (J mol^{-1}), R – the gas constant (J mol^{-1} K^{-1}) $f(\alpha)$ and $g(\alpha)$ – the differential and integral functions, respectively.

Experimental

Preparation of the compound

Analytical grade $NaBPh_4$, N,N-dimethylamine, *t*-butylbromide and cyclohexylbromide were used as received. Ether (AR) was treated with $FeSO_4$ solution and distilled at 307.9 K (n_D^{20}=1.2652). Deionized water was redistilled (conductivity $1.19 \cdot 10^{-4}$ S m^{-1}).

Preparation of N,N-dimethylcyclohexylamine. N,N-dimethylcyclohexylamine was prepared according to the method of literature [4, 5].

Preparation of cyclohexyl-*t*-butyldimethylammonium bromide. 0.05 mol *t*-butylbromide was added dropwise to a stirred solution of 0.05 mol N,N-dimethylcyclohexylamine in 7 ml of methanol maintained at 0°C. The icebath was removed and the reaction mixture was stirred 3 h at 40°C, the solution was then poured into 20 ml of ether, filtered, and washed with ether. Dry it at room temperature in a KOH vacuum desiccator for 7 days before use [6]. Analysis for cyclohexyl-*t*-butyldimethylammonium bromide $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]Br$ is as follows C: 54.69(54.57); H: 9.74(9.85); N: 5.24(5.30).

Preparation of cyclohexyl-t-butyldimethylammonium tetraphenylborate. The compound was prepared by the addition of a 5% excess of freshly prepared 0.01 mol l^{-1} sodium tetraphenylborate solution to a 0.01 mol l^{-1} solution of cyclohexyl-t-butyldimethylammonium boride. The resultant precipitate was allowed to stand 20 min and was then filtered, and washed several times with water. The compound was recrystallized from an acetone-water (3:1 v/v) solution. Dry it at room temperature in a vacuum desiccator for 6 days. Analysis for cyclohexyl-t-butyldimethylammonium tetraphenylborate $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4$ is as follows: C: 86.13(85.92); H: 9.01(9.15); N: 2.84(2.78); B: 2.21(2.15).

Physical measurement

TG analysis was carried out on a Perkin Elmer TGA-7 thermogravimetric analyzer at an O_2 flow rate of 60 ml min^{-1} and a heating rate 5.00 deg min^{-1}. The amount of sample used was 2.666 mg, and the temperature range was 40 to 370°C.

UV spectra were recorded on a Shimadzu 265 spectrometer. IR spectra of the products of thermal decomposition were examined on a Shimadzu 403 infrared spectrophotometer (KBr plates, 4000~650 cm^{-1}) at every stage.

Component analysis

BPh_4^- ions content in tetraphenylborate was determined according to the reported general procedure [7]. C, H and N content were determined by using a Perkin Elmer 240 elemental analyzer.

Result and discussion

Thermal decomposition process

The TG-DTG curves are shown in Fig. 1. The TG-DTG curves indicate that the compound undergoes a three-stage oxidative decomposition process, one fast oxidative stage, and two slow oxidative stages.

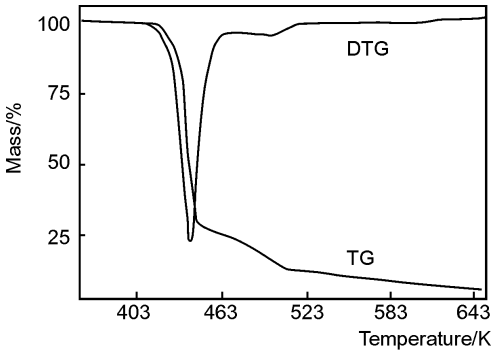

Fig. 1 TG and DTG curves of $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4$

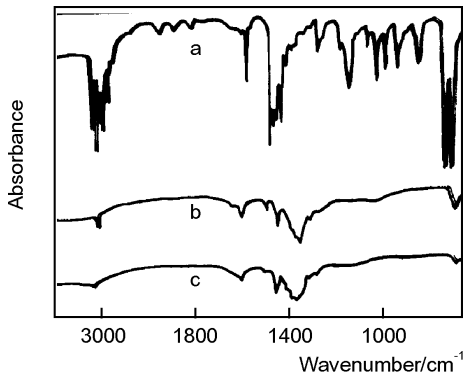

Fig. 2 IR spectra of (a) $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4$, (b) product of decomposition up to 456 K, and (c) product of decomposition up to 509 K

Table 1 Function forms used for present analysis

Function No.	$f(\alpha)$	$g(\alpha)$
1	$1/(2\alpha)$	α^2
2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
3	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2/3\alpha)-(1-\alpha)^{2/3}$
4	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
5	$3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^2$
6	$3/2(1-\alpha)^{4/3}[\{1/(1-\alpha)^{1/3}-1\}]^{-1}$	$[\{1/(1-\alpha)^{1/3}-1]^2$
7	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
8	$(1-\alpha)$	$-\ln(1-\alpha)$
9–12	$(1/n)(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$	$[-\ln(1-\alpha)]^n$
	n=(2/3, 1/2, 1/3, 1/4)	
13–14	$n(1-\alpha)^{(n-1)/n}$	$1-(1-\alpha)^{1/n}$
	n=(2, 3)	
15–18	$(1/n)\alpha^{-(n-1)}$	α^n
	n=(1, 1/2, 1/3, 1/4)	
19	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
20	$(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$
21–23	$(1/n)(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$	$[-\ln(1-\alpha)]^n$
	n=(2, 3, 4)	
24	$1/2(1-\alpha)^3$	$[1/(1-\alpha)]^2-1$
25	$4(1-\alpha)^{3/4}$	$1-(1-\alpha)^{1/4}$
26	$6[1-(1-\alpha)^{1/3}]^{1/2}(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]^{1/2}$
	$4[1-(1-\alpha)^{1/2}]^{1/2}(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]^{1/2}$
28–30	$(1/n)(1-\alpha)^{-(n-1)}$	$1-(1-\alpha)^n$
	n=(2, 3, 4)	

The IR spectra of the products of thermal decomposition at various stages were examined in Fig. 2. The IR spectrum of the residue after decomposition up to 456 K is much different from that of cyclohexyl-t-butyldimethylammonium tetraphenylborate. The IR absorption peaks of γ_{C-H} (2850~2950), δ_{CH_3} (1485), δ_{CH_2} (1469 cm^{-1}) of alkyl, and the peaks of $C(CH_3)_3$ skeleton vibration (1273, 1257 cm^{-1}) are all lost. But the IR absorption peaks of γ_{C-H} (3050 cm^{-1}), C=C and C=C (1603, 1500, 1449 cm^{-1}) of phenyls are still observed. Several new peaks of γ_{B-O} and γ_{B-O-B} in the region 1250~4000 cm^{-1} are also observed.

This shows that phenyls are still present in the tested substance, but cyclohexyl-t-butyldimethyl ammonium ion is not. With the TG curves, the probable product of decomposition at this stage is $B_4O_3Ph_6$ (mass loss: calc. 72.49, found 72.40%).

The IR spectrum of the product of decomposition up to 509 K is similar to that of the residue $B_4O_3Ph_6$. The peaks of C=C and C=C of phenyls at 1600, 1450 cm^{-1} and the peaks of γ_{B-O} and γ_{B-O-B} in the region of 1250~1400 cm^{-1} exist yet. TG studies show that the probable product at this stage is $B_4O_5Ph_2$ (mass loss: calc. 86.22, found 85.98%).

The final oxidative decomposition substance is considered to be B_2O_3 (mass loss: calc. 93.08 found 92.95%). It was also confirmed by a chemical analysis method, when a solution of carminic acid of dense sulfuric acid was added to the residue, a red solution was changed into a blue solution.

Biphenyl was definitely indicated in the effluent gas mixtures in the first and the second decomposition stages, respectively, UV absorption maxima at 334 nm and the region of 240~260 nm, characteristic of biphenyl, was observed in the ethanol solution of this mixture gases.

These results suggested a possible decomposition process of cyclohexyl-t-butyldimethylammonium tetraphenylborate under O_2 condition as following:

$$[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4 \xrightarrow{375\text{–}456\ K} B_4O_3Ph_6 \xrightarrow{456\text{–}509\ K}$$

$$B_4O_5Ph_2 \xrightarrow{509\text{–}543\ K} B_2O_3$$

Non-isothermal kinetic studies for the first decomposition process

The possible forms of $f(\alpha)$ and $g(\alpha)$ are listed in Table 1. The original data on the first decomposition process of cyclohexyl-t-butyldimethylammonium tetraphenylborate are listed in Table 2.

Table 2 TG-DTG data on the thermal decomposition of $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4$

No.	T/K	α	$d\alpha/dt$
1	418.27	0.03185	0.0333
2	421.52	0.05135	0.0638
3	424.22	0.0766	0.0952
4	427.47	0.1216	0.1543
5	430.17	0.1778	0.2476
6	433.42	0.2814	0.3857
7	436.66	0.4414	0.5905
8	439.36	0.6015	0.8190
9	441.53	0.8075	1.0286
10	442.61	0.8938	0.9428

Using the possible forms of $g(\alpha)$ and $f(\alpha)$ in Table 1, the data in Table 2 are analyzed by use of Eqs (1) and (2). For Eqs (1) and (2), the kinetic analysis is completed by the linear least square method on a computer. The results are shown in Table 3.

Table 3 Results of kinetic analysis of $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4$ in the first decomposition process

Function	Differential method			Integral method		
No.	$\ln A/S^{-1}$	E/kJ mol^{-1}	r	$\ln A/S^{-1}$	E/kJ mol^{-1}	r
1	117.47	429.28	0.9987	113.63	417.75	0.9999
2	130.75	478.43	0.9999	120.89	445.47	0.9999
3	134.99	498.63	0.9995	122.60	456.65	0.9997
4	145.91	537.07	0.9969	129.16	479.57	0.9986
5	103.80	389.15	0.9960	103.38	389.81	0.9994
6	159.57	585.11	0.9922	151.16	556.44	0.9907
7	88.35	323.05	0.9978	84.51	311.52	0.9999
8	91.88	332.13	0.9868	69.45	254.45	0.9954
9	67.59	244.93	0.9825	45.15	167.24	0.9952
10	55.36	201.32	0.9786	32.90	123.62	0.9950
11	43.01	157.72	0.9718	20.53	80.03	0.9947
12	36.76	135.91	0.9663	14.24	58.23	0.9945
13	74.80	274.47	0.9980	61.07	227.78	0.9994
14	79.86	293.69	0.9949	63.08	236.18	0.9985
15	59.11	216.81	0.9956	55.26	205.29	0.9999
16	29.58	110.58	0.9852	25.69	99.05	0.9999
17	19.56	75.17	0.9701	15.64	63.65	0.9999
18	14.47	57.47	0.9516	10.50	45.92	0.9997
19	124.65	447.44	0.9608	88.48	320.61	0.9766
20	107.57	389.78	0.9734	12.57	50.46	0.8041
21	164.22	593.75	0.9913	141.81	516.08	0.9955
22	236.27	855.37	0.9928	213.85	777.69	0.9955
23	308.21	1117.00	0.9935	285.79	1039.28	0.9955
24	158.12	562.56	0.9403	112.28	401.20	0.9511
25	85.07	303.30	0.9931	64.06	240.56	0.9978
26	46.48	172.00	0.9908	29.68	114.50	0.9983
27	42.42	156.99	0.9960	28.65	110.30	0.9993
28	27.02	101.50	0.7303	45.88	170.59	0.9939
29	–5.34	–13.80	0.0811	38.98	145.58	0.9829
30	–37.82	–129.12	0.4673	33.75	126.75	0.9707

A method of selection of the most probable function of thermal decomposition mechanism was suggested by Zhanghuai *et al.* [8] on the basis of comparison of kinetic parameters values of E and A obtained by use of Eqs (1) and (2) among those functions which have better coefficients. This method was also used to conclude the function of decomposition mechanism of some compounds in our previous papers [9, 10]. According to this, only No. 5 in Table 3 has approximately the same values of E and $\ln A$ between the two equations, and the coefficients are also good. Thus the most probable function of mechanism of the first oxidative decomposition stage of $[C_6H_{11}N(CH_3)_2(C(CH_3)_3)]BPh_4$ can be concluded as the function of No. 5 in Table 1. The kinetic equation of this stage is

$$d\alpha/dt = A\exp(-E/RT)3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$$

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