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Kinetic study of orthoboric acid decomposition by inverse thermal analysis (CDRTA)

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Abstract

The thermal decomposition reactions in a vacuum of orthoboric acid, $B(OH)_3$, were studied by means of inverse thermal analysis (constant-rate thermal analysis). This method allows us to establish unambiguously the kinetic equations governing these processes and to determine the kinetic parameters.

INTRODUCTION

Inverse thermal analysis (ITA) is the term proposed by Rouquerol for constant-rate decomposition thermal analysis [1]. In this technique, the temperature is followed with respect to the time, i.e. with respect to the mass variation, because the decomposition rate is constant. In this way, an inverse representation is obtained, hence the proposed name of the technique.

The dehydration processes in air of orthoboric acid have been studied by Gordillo et al. [2]. However, there is some discussion in the literature concerning the occurrence of tetraboric acid, $H_2B_4O_7$, in these reactions, and therefore inverse thermal analysis appears to be an ideal technique for the study of these dehydration reactions.

It appears that the structure of the metaboric acid formed during the decomposition determines whether or not tetraboric acid is formed. In this way, orthorhombic metaboric acid, whose B atoms are equivalent, can dehydrate directly to B_2O_3, while the monoclinic variety [3], in which the B atoms are not equivalent, yields tetraboric acid as an intermediate reaction product. In air, decomposition of $B(OH)_3$ gives the orthorhombic form of metaboric acid, while in a vacuum the monoclinic form is produced.

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EXPERIMENTAL

Thermal runs were performed on ITA equipment made in our laboratory according to the instructions given by Rouquerol [1]. It consists of a furnace controlled by a pressure signal that comes from a Pirani manometer that measures the pressure in the reaction chamber. While keeping the pressure constant, the heating rate is controlled, thus maintaining the decomposition rate constant.

Orthoboric acid was supplied by Merck (r.p.a), and the total decomposition pressure was in the range 10^{-2} to 4×10^{-2} mmHg.

RESULTS AND DISCUSSION

Figure 1 shows a characteristic decomposition curve, in which five zones can be distinguished.

(i) At first the temperature and pressure increase, and when the pre-fixed pressure is reached, the temperature regulation of the furnace is initiated.

(ii) The pressure is maintained constant and the temperature increase is slow.

(iii) A sudden temperature increase and pressure drop indicate the end of the reaction.

(iv) A new decomposition process starts up and the pressure reaches the fixed value; the temperature increases again until the end op the reaction.

(v) The end of the reaction causes a decrease in pressure and a large increase in temperature. The thermal run is then complete.

Table 1 shows the seven kinetic equations used for the kinetic analysis [4], and in Tables 2–4 the results obtained for the first decomposition reaction

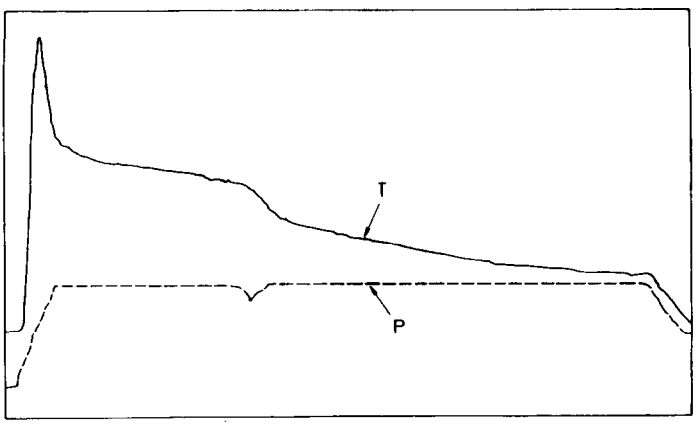

Fig. 1. Experimental ITA curves for the dehydration of orthoboric acid: *T*, temperature; *P*, pressure versus time.

TABLE 1

Equations used for the kinetic analysis

No.	$f(\alpha)$	Mechanism
1	$1/2$	D1 One-dimensional diffusion
2	$(-\ln(1-\alpha))-1$	D2 Two-dimensional diffusion
3	$\frac{3/2(1-\alpha)2/3}{1-(1-\alpha)1/3}$	D3 Three-dimensional diffusion (Jander equation)
4	$[3/2(1-\alpha)-1/3]-1$	D4 Three-dimensional diffusion (Ginstling–Brounhstein eqn.)
5	$(1-\alpha)$	F1 Random nucleation
6	$2(1-\alpha)1/2$	R2 Contracting cylinder
7	$3(1-\alpha)2/3$	R3 Contracting sphere

TABLE 2

Data corresponding to the first decomposition of $B(OH)_3$ (reaction rate, C)

α	T (K)	α	T (K)
0.20	344.0	0.55	346.9
0.25	344.3	0.60	347.5
0.30	344.7	0.65	348.2
0.35	345.1	0.70	349.0
0.40	345.5	0.75	349.9
0.45	345.9	0.80	351.0
0.50	346.4		

TABLE 3

Data corresponding to the first decomposition of $B(OH)_3$ (reaction rate, $C/5.038$)

α	T (K)	α	T (K)
0.20	328.8	0.55	331.5
0.25	329.1	0.60	332.0
0.30	329.4	0.65	332.5
0.35	329.7	0.70	333.3
0.40	330.1	0.75	334.2
0.45	330.5	0.80	335.2
0.50	331.0		

of $B(OH)_3$ at three different rates of decomposition, C, $C/5.038$ and $C/8.602$, are shown.

Kinetic analysis is very easy under these conditions. Assuming the general equation

$$d\alpha/dt = A \exp(-E/RT) f(\alpha) \quad (1)$$

TABLE 4

Data corresponding to the first decomposition of $B(OH)_3$ (reaction rate, $C/8.602$)

α	T (K)	α	T (K)
0.20	324.0	0.55	326.5
0.25	324.3	0.60	327.1
0.30	324.6	0.65	327.7
0.35	325.0	0.70	328.4
0.40	325.3	0.75	329.1
0.45	325.7	0.80	330.2
0.50	326.1		

given that $d\alpha/dt$ = constant, then

$$C/A = \exp(-E/RT)f(\alpha) \tag{2}$$

and hence

$$\ln(C/A) = -E/RT + \ln f(\alpha) \tag{3}$$

and

$$\ln f(\alpha) = \ln(C/A) + E/RT \tag{4}$$

In consequence, a plot of $\ln f(\alpha)$ vs. $1/T$ will be a straight line of slope E/R. The results of these representations are given in Table 5. Because the correlation coefficients are near to unity, the mechanisms cannot be distinguished on the basis of these representations.

Nevertheless, we can use these results in another way: from eqn. (2), for two decomposition rates C_1 and C_2

$$C_1/A = \exp(-E/RT_1)f(\alpha) \tag{5}$$

and

$$C_2/A = \exp(-E/RT_2)f(\alpha) \tag{6}$$

TABLE 5

Results obtained from the representation of eqn. (4) ($B(OH)_3 \rightarrow HBO_2 + H_2O$) at different reaction rates

Mechanism	C			$C/5.038$			$C/8.602$		
	r	i	s	r	i	s	r	i	s
D1	0.919	−55.13	19153.1	0.934	−67.06	22245.3	0.932	−68.51	22392.2
D2	0.958	−83.48	29101.8	0.965	−97.47	32431.9	0.962	−99.54	32630.9
D3	0.968	−94.18	33288.6	0.972	−108.70	36594.5	0.969	−111.00	36815.2
D4	0.978	−117.30	41222.4	0.981	−132.90	44529.0	0.978	−135.70	44793.9
F1	0.997	−69.39	23794.6	0.999	−72.63	23805.8	0.996	−74.07	23926.9
R2	0.997	−34.00	11897.3	0.999	−35.62	11902.9	0.996	−36.34	11964.6
R3	0.997	−45.16	15863.4	0.999	−47.32	15872.0	0.996	−48.29	15953.1

Key: i, intercept value; s, slope.

TABLE 6

Values of E/R calculated from the observed temperature differences at various values of α = constant for the first stage of the decomposition of $B(OH)_3$

α	Reaction rate relationship		
	5.038/1	8.602/5.038	8.602/1
0.20	12032.6	11873.5	11992.6
0.25	12054.0	11205.8	12014.2
0.30	12000.1	11226.4	11979.4
0.35	11946.9	12196.8	12008.1
0.40	11975.3	11968.2	11973.5
0.45	12003.7	11997.5	12002.1
0.50	12039.2	11784.9	11975.0
0.55	12074.8	11580.8	11948.1
0.60	12035.8	11856.7	11990.8
0.65	11924.3	12144.2	11978.2
0.70	11980.5	11950.5	11973.0
0.75	12043.8	11537.4	11913.8
0.80	12041.1	11842.8	11991.2
Average	12011.7	11782.0	11980.0

In consequence

$$\ln(C_1/C_2) = E/R(1/T_1 - 1/T_2) \quad (7)$$

Equation (7) shows that we can obtain the activation energy value from the temperatures corresponding to the same degree of reaction at two reaction rates, C_1 and C_2.

Table 6 shows the results of this analysis. We see that a value of around 12 000 K is obtained for the E/R parameter and thus an R2 mechanism can be selected unambiguously from Table 5. In this way, combining both analysis methods, an easy determination of the mechanism and kinetic parameters can be performed.

A similar study was made for the second decomposition stage. Tables 7–9 list the decomposition data for rates of C, $C/5.038$ and $C/8.602$. Analysis

TABLE 7

Data corresponding to the second decomposition stage of $B(OH)_3$ (reaction rate, C)

α	T (K)	α	T (K)
0.20	381.8	0.55	384.7
0.25	382.1	0.60	385.4
0.30	382.4	0.65	386.1
0.35	382.8	0.70	386.8
0.40	383.2	0.75	387.8
0.45	384.6	0.80	389.0
0.50	384.2		

TABLE 8

Data corresponding to the second decomposition stage of $B(OH)_3$ (reaction rate, $C/5.038$)

α	T (K)	α	T (K)
0.20	365.8	0.55	368.5
0.25	366.1	0.60	369.1
0.30	366.4	0.65	369.7
0.35	366.7	0.70	370.4
0.40	367.1	0.75	371.3
0.45	367.5	0.80	372.4
0.50	368.0		

TABLE 9

Data corresponding to the second decomposition stage of $B(OH)_3$ (reaction rate, $C/8.602$)

α	T (K)	α	T (K)
0.20	360.7	0.55	363.4
0.25	361.0	0.60	363.9
0.30	361.3	0.65	364.5
0.35	361.6	0.70	365.2
0.40	362.0	0.75	366.1
0.45	362.4	0.80	367.1
0.50	362.9		

according to eqn. (4) is shown in Table 10 and once again the correlation coefficients cannot discriminate the kinetic mechanism. Nevertheless, the obtained value of 14000 K for the E/R parameters, (Table 11) indicates clearly an R2 mechanism (see Table 10).

TABLE 10

Results obtained from the representation of eqn. (4) ($HBO_2 \rightarrow B_2O_3 + H_2O$) at different reaction rates

Mechanism	C			$C/5.038$			$C/8.602$		
	r	i	s	r	i	s	r	i	s
D1	0.929	−68.31	26303.9	0.934	−72.37	26688.3	0.932	−73.12	26588.2
D2	0.960	−99.37	38379.4	0.965	−105.30	38934.1	0.963	−106.30	38773.5
D3	0.968	−110.80	43314.8	0.973	−117.50	43937.2	0.971	−118.70	43752.9
D4	0.977	−135.60	52725.4	0.982	−143.70	53485.1	0.979	−145.10	53243.7
F1	0.997	−74.16	28225.6	0.999	−78.49	28626.7	0.999	−79.18	28477.7
R2	0.997	−36.39	14113.9	0.999	−38.55	14313.1	0.999	−38.90	14239.4
R3	0.997	−48.35	18819.2	0.999	−51.22	19084.1	0.999	−51.69	18985.9

Key: i, intercept value; s, slope.

TABLE 11

Values of E/R calculated from the temperature differences at various values of α = constant for the second decomposition stage of $B(OH)_3$

α	Reaction rate relationship		
	5.038/1	8.602/5.038	8.602/1
0.20	14114.7	13840.8	14045.6
0.25	14137.4	13864.7	14068.3
0.30	14160.1	13886.6	14091.1
0.35	14098.4	13909.6	14051.0
0.40	14128.5	13940.1	14081.2
0.45	14158.7	13970.7	14111.5
0.50	14112.5	14009.0	14086.6
0.55	14150.0	13773.4	14054.5
0.60	14111.7	13818.6	14037.7
0.65	14074.0	13863.9	14021.2
0.70	14126.2	13916.8	14073.6
0.75	14111.1	13985.5	14079.6
0.80	14111.2	13899.4	14032.4
Average	14122.7	13898.4	14064.2

We conclude that the proposed ITA method permits the unambiguous selection of the kinetic equation and kinetic parameters for a given decomposition process.

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