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KINETIC ANALYSIS OF THERMAL DECOMPOSITION REACTIONS. I. THERMAL DECOMPOSITION OF POTASSIUM BROMATE

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ABSTRACT

The kinetics of the thermal decomposition of potassium bromate were studied using isothermal and dynamic thermogravimetric techniques. Kinetic analysis of isothermal data in view of various solid-state reaction models showed that the reaction is best described by phase-boundary controlled and random nucleation models. Kinetic analysis of dynamic TG curves were discussed and a critical comparison was made of three methods: the direct differential method and two integral methods, one of Coats and Redfern and the other of Ozawa. The results showed that the Ozawa method gives better correlation and the results are in good agreement with those obtained under isothermal thermogravimetric conditions.

INTRODUCTION

Processes involving the chemical transformations of solids play an increasingly important role in modern technology, as sophisticated and costly solids can be produced by reactions of other, precursory solids. To obtain the desired purity, structure and texture of the material, a very careful control of the reaction is necessary [1]. There is considerable diversity of mechanisms by which solids react and there are a variety of factors which may control, determine, influence or modify the rate limiting processes. In many cases, the kinetics of thermal decomposition reactions were followed, depending on the system investigated, by measurements of pressure changes and by analysis of products by mass spectrometry. However, more recently, DTA–TG analytical techniques are more widely used, since they provide a rapid and convenient method for the quantitative investigation of decomposition reactions [2].

Several approaches have been used to calculate the kinetic parameters from the experimental data. A comparison of the fractional reaction (α)–time

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curves, measured for a particular reaction, with theoretical expressions, derived for appropriate nucleation and growth models, has been widely used as evidence for the identification of the geometry of interface advance. Although the theoretical basis of the equations used in the interpretation of dynamic TG data has been questioned in the literature, several examples of close agreement between isothermal and dynamic methods have been reported. Non-isothermal data are dependent on the heating rate and are subject to possible inaccuracies due to the influence of sample size and shape on heat flow and for these reasons isothermal kinetic measurements are, in general, the more reliable [3].

In the present study, the kinetics of the isothermal and non-isothermal decomposition of potassium bromate crystals were investigated. Jach [4] studied the isothermal decomposition reaction of potassium bromate crystals by pressure measurements in a closed system, and reported that the reaction follows an exponential law over most of the decomposition. In studying the thermal decomposition of $NaBrO_3$ [5], it was proposed that the product growth is controlled by phase boundary reaction for a contracting cube reacting from the edge inward.

EXPERIMENTAL

Potassium bromate (A.R.) was recrystallized from bidistilled water and dried at 150°C for few hours, then sieved to obtain crystals in the 80–100 mesh range.

The kinetics of the thermal decomposition of $KBrO_3$ crystals were investigated using isothermal and dynamic TG techniques. In the isothermal

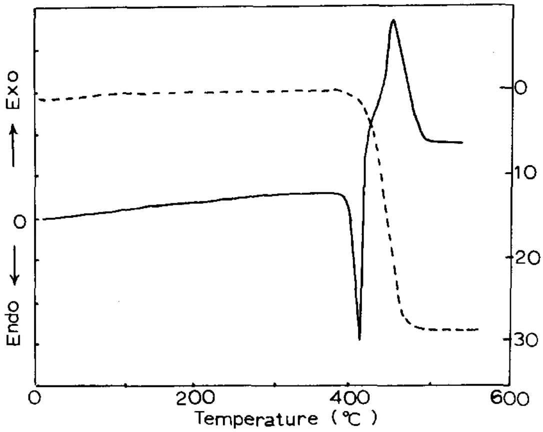

Fig. 1. DTA (———) and TG (- - - - - -) curves of $KBrO_3$.

studies the reaction temperature was varied between 360 and 422°C and to ensure linear heating rates and accurate temperature measurements, the sample weights were about 6–7 mg. DTA–TG studies showed that potassium bromate loses weight in one step to yield potassium bromide and oxygen. Figure 1 shows the DTA and TG curves obtained at a heating rate 20°C min^{-1}. The DTA curve shows an endothermic peak at 410°C due to melting followed by an exothermic peak at 450°C due to decomposition. The TG curve showed for complete decomposition a weight loss which amounts to about 28.7%, in agreement with the calculated value.

RESULTS AND DISCUSSION

Figure 2 shows typical α/t curves for the isothermal decomposition of $KBrO_3$ crystals. Under isothermal conditions, the rate constant, k, is independent of reaction time and so $kt = g(\alpha)$. A plot of $g(\alpha)$ vs. time should thus give a straight line if the correct form of $g(\alpha)$ is used. Table 1 lists some of the more important kinetic equations given in the literature [6–8] which were examined in the present study in order to find the most appropriate kinetic expression and reaction model which describe the reaction.

The function $g(\alpha)$ depends on the mechanism controlling the reaction and on the size and shape of the reacting particles. In diffusion-controlled reactions, D_1 is for a one-dimensional diffusion process governed by a parabolic law, with constant diffusion coefficient; D_2 is a two-dimensional diffusion-controlled process into a cylinder; D_3 is Jander's equation for a diffusion-controlled reaction in a sphere, and D_4 is the function for a diffusion-controlled reaction starting on the exterior of a spherical particle.

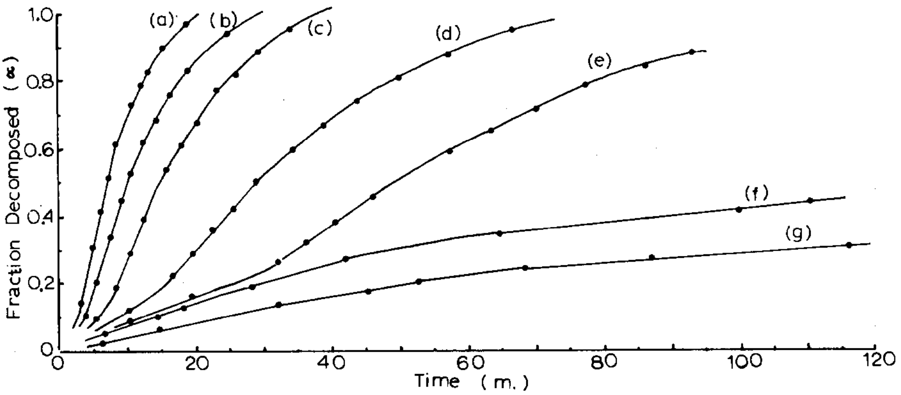

Fig. 2. Isothermal α/t curves for decomposition of $KBrO_3$: (a) 417; (b) 409; (c) 400; (d) 390; (e) 381; (f) 371 and (g) 363°C.

TABLE 1

Kinetic equations examined in this work

Reaction model	$g(\alpha)$	Function symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2
Jander equation, three-dimensional diffusion	$\{1-(1-\alpha)^{1/3}\}^2$	D_3
Ginstling–Brounshtein equation, three-dimensional diffusion	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$\{1-(1-\alpha)^{1/2}\}$	R_2
Three-dimensional phase boundary reaction	$\{1-(1-\alpha)^{1/3}\}$	R_3
First-order kinetics	$\{-\ln(1-\alpha)\}$	F_1
Random nucleation: Avrami equation	$\{-\ln(1-\alpha)\}^{1/2}$	A_2
Random nucleation: Erofeev equation	$\{-\ln(1-\alpha)\}^{1/3}$	A_3

If the reaction is controlled by movement of an interface at constant velocity and nucleation occurs virtually instantaneously, then for such phase-boundary controlled reactions, equations relating α and t are the R_2 function for a circular disc reacting from the edge inward and the function R_3 for a sphere reacting from the surface inward. If the solid state reaction follows first-order kinetics (F_1 function), then the rate-determining step is the nucleation process and there is equal probability of nucleation at each active site. In phase-boundary reactions, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particle is covered with a layer of product. Nucleation of the reactant, however, may be a random process, not followed by rapid surface growth. As nuclei grow larger they must eventually impinge on one another, so that growth ceases where they touch. This process has been considered by Avrami and by Erofeev, who have given the functions A_2 and A_3, respectively.

The isothermal α/t data were analyzed according to the various kinetic equations by the regression analysis and the comparison of fits given in Table 2, shows that the best fit of data is obtained with phase-boundary controlled reactions (R_2 and R_3 functions) and the random nucleation model (A_2 function). Based on the R_3 model, typical plots of $(1-(1-\alpha)^{1/3})$ vs. time in the temperature range 380–420°C are shown in Fig. 3. At lower temperatures ($T < 380$°C), the decomposition rates were much lower than expected from measurements made at the higher temperatures. Figure 1 showed that melting precedes decomposition and microscopic examination [4] revealed that surface pre-melting could take place and thus the kinetic

TABLE 2

Comparison of fit of various kinetic models to the isothermal results in the thermal decomposition of $KBrO_3$ crystals

Function symbol	Temperature (°C)				
	381	390	400	409	417
D_1	0.9922	0.9952	0.9941	0.9940	0.9972
D_2	0.9799	0.9877	0.9856	0.9958	0.9952
D_3	0.9550	0.9525	0.9476	0.9729	0.9783
D_4	0.9724	0.9790	0.9762	0.9914	0.9913
R_2	0.9994	0.9992	0.9985	0.9966	0.9973
R_3	0.9975	0.9981	0.9976	0.9988	0.9996
F_1	0.9888	0.9828	0.9808	0.9987	0.9969
A_2	0.9993	0.9992	0.9977	0.9913	0.9951
A_3	0.9960	0.9928	0.9888	0.9780	0.9867

parameters obtained at lower temperatures differ from those at the higher temperatures.

Figure 4 shows representative weight changes as a function of temperature from dynamic measurements of $KBrO_3$ thermal decomposition. In view of the conclusions from isothermal studies, only the nucleation models should be used to analyze the results. In the analysis of dynamic TG curves we assumed R_3 function (which gave the highest correlation coefficient) and made a critical comparison of three dynamic methods: a direct differential

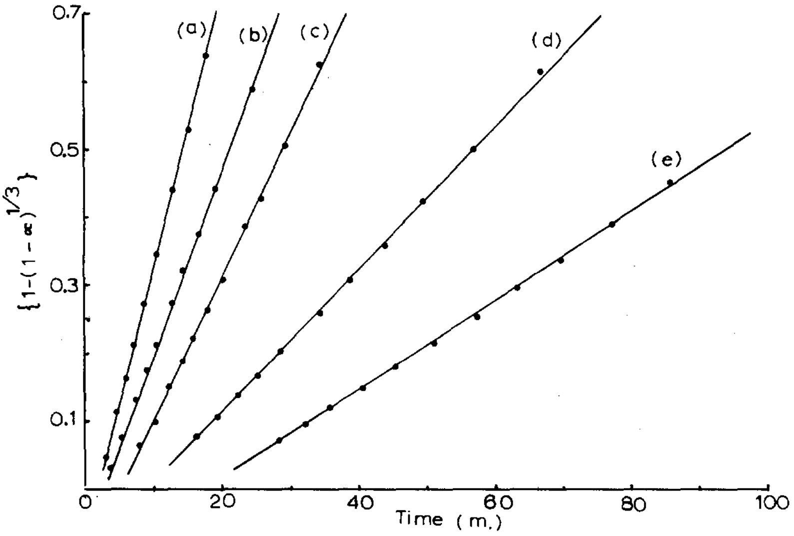

Fig. 3. Isothermal decomposition of $KBrO_3$ according to the three-dimensional phase-boundary reaction model: (a) 417; (b) 409; (c) 400; (d) 390 and (e) 381°C.

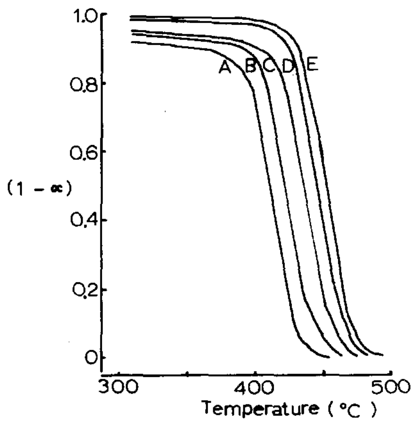

Fig. 4. Typical weight changes from dynamic measurements for $KBrO_3$ thermal decomposition. Heating rate: (A) 2.0; (B) 5.0; (C) 10.0; (D) 15.0 and (E) 20.0°C min^{-1}.

method [3] and two integral methods, one of Coats and Redfern [9,10] and the other of Ozawa [11]. In the first method, the rate of change of the fraction of material (α) with respect to temperature is expressed according to the equation:

$$\ln\,(\mathrm{d}\alpha/\mathrm{d}T)\beta/\mathrm{f}(\alpha) = \ln\,A - (E/RT)$$

where $\mathrm{f}(\alpha)$ depends upon the reaction mechanism, β is the rate of temperature change, A is the frequency factor and E is the activation energy of the reaction. In the Coats and Redfern method, to allow for the calculation of the activation energy, the correct form of $\mathrm{g}(\alpha)$ is used in the equation:

$$-\ln\,\mathrm{g}(\alpha)/T^2 = -\ln(AR/\beta E)(1-2RT/E) + (E/RT)$$

The quantity $\ln(AR/\beta E)(1-2RT/E)$ appears to be reasonably constant for most values of E and in the temperature range over which most reactions occur. In the Ozawa approximate integral method, a master curve may be derived from the thermogravimetric data obtained at different heating rates, and the result is:

$$AE/R\beta_1\mathrm{P}(E/RT_1) = AE/R\beta_2\mathrm{P}(E/RT_2) = \ldots$$

where the function $\mathrm{P}(E/RT)$ was approximated by the equation:

$$\log\,\mathrm{P}(E/RT) = -2.315 - 0.4567(E/RT)$$

Hence the activation energy was calculated from the thermogravimetric curves obtained at different heating rates. The frequency factor was determined by the subtraction of $\log(E/\beta R)$ $\mathrm{P}(E/RT)$ from $\int \mathrm{d}(1-\alpha)/\mathrm{f}(1-\alpha)$ of the determined form of $\mathrm{f}(1-\alpha)$. Table 3 shows the results of the calculation of the kinetic parameters for these three methods assuming that the reaction obeys the R_3 model.

TABLE 3

Kinetic parameters for R_3 model calculated according to isothermal and dynamic methods

Method of analysis	Heating rate (°C min^{-1})	E (kJ mol^{-1})	Log A (min^{-1})	Correlation coefficient
Isothermal		193.3	13.3	0.994
Dynamic				
(a) Direct differential	5	178.9	12.17	0.968
	10	255.5	17.79	0.984
	15	259.5	17.97	0.938
	20	276.3	19.12	0.980
(b) Coats and Redfern	5	233.1	16.24	0.989
	10	204.1	14.04	0.989
	15	249.4	17.31	0.993
	20	272.6	18.98	0.996
(c) Ozawa		210 ± 8	15.1 ± 0.2	

Dollimore et al. [13,14] reported more than one straight line from the analysis of TG dynamic experiments using the direct differential method, and this was attributed to the variation in the distribution of reaction sites as the reaction proceeds from one distribution of sites to the other. Sharp and Wentworth [10] made a comparative study between differential methods and the Coats and Redfern integral method in studying the decomposition of $CaCO_3$ and concluded that the Coats and Redfern method leads to more satisfactory kinetic analyses.

The results obtained in the present study show that the Ozawa method gives a more satisfactory kinetic analysis than that of Coats and Redfern and much more so than the direct differential method. Correlation coefficients depended to a large extent on the number of data points taken in the regression analysis. We have used data points covering the range $0.05 < \alpha < 0.95$. The direct differential method is the least satisfactory and gave results which differ widely from the results obtained under isothermal conditions and have the least correlation. The Coats and Redfern method is less tedious to apply to the TG data and avoids the determination of tangents, but the results obtained are still not accurate enough and do not compare well with the results of the isothermal kinetic analysis. On the other hand, the Ozawa method of analysis gave more accurate results with better correlation and better agreement with the results obtained under isothermal TG kinetic analysis. A single activation energy and frequency factor is obtained instead of a wide range of values obtained at different heating rates. It allows comparisons to be made between different dynamic results obtained under different conditions.

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