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IRON COMPOUNDS IN HIGH OXIDATION STATES. III. * KINETIC ANALYSIS OF THE REACTION BETWEEN BaO_2 AND $FeSO_4$: NON-ISOTHERMAL VERSUS ISOTHERMAL PROCEDURES

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ABSTRACT

The formal kinetic analysis of the reaction between BaO_2 and $FeSO_4$ yielding $BaFeO_3$ has been carried out using thermogravimetric data. The comparative study of non-isothermal and isothermal procedures allows one to establish that only a single TG curve would be required to determine the mechanism type and the kinetic parameters for reactions occurring in a unique stage.

INTRODUCTION

Both isothermal and non-isothermal procedures have long been employed to carry out solid-state reaction kinetic analysis. Each one of these two basic working methods has advantages and limitations which have been widely argued (see, e.g., [1–3]). A great number of models have been developed to evaluate the experimental kinetic data. Likewise, in order to extract kinetic parameters, mathematical approaches have also been established that obviate the question of which is the rate controlling process [4].

Nevertheless, whereas there is a great deal of illustrative applications of all these tools in the study of solid thermal degradation reactions, the information on their reliability when applied to other more complex reactions involving solids is comparatively scarce.

As we have reported in a recent publication [5], the reaction between BaO_2 and $FeSO_4$ leads to the formation of a definite Fe(IV) phase according to

$$2BaO_2 + FeSO_4 \xrightarrow[370°C]{N_2} BaFeO_3 + BaSO_4 + 1/2O_2\uparrow$$

The O_2 evolution implied by this reaction allows one to follow its course by means of thermogravimetric techniques.

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* For Parts I and II of this work, see Thermochimica Acta, 91 (1985) 249 and 97 (1986) 243, respectively.

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Our present paper summarizes the results from the kinetic analysis of the above reaction. Non-isothermal and isothermal procedures have been used and the kinetic data obtained have been compared. In so doing,we have a double aim: first, we try to gain an understanding of the mechanism through which such a reaction occurs and, secondly, by means of the comparative evaluation of the results, it is possible to gain further insight on the suitability of the non-isothermal procedures to the study of complex solid state reactions.

EXPERIMENTAL

Samples containing the stoichiometric $BaO_2/FeSO_4$ ratio were prepared as previously described [5].

The weight loss data to perform the non-isothermal kinetic analysis were extracted from a single TG curve obtained (using a Setaram instrument [5]) under the following conditions: sample mass, 196.90 mg; heating rate, 0.73°C min^{-1}; dynamic N_2 atmosphere.

Isothermal experiments were carried out under dynamic N_2 atmosphere on samples accurately weighed (ca. 200 mg) at 328, 340, 346 and 359°C.

RESULTS AND DISCUSSION

Non-isothermal kinetics

The data couples "fraction of reaction (α)–temperature" provided by the TG curve are summarized in Table 1 *. From these, we have analyzed the more widely assumed models for the kinetic study of solid state reactions [3],

TABLE 1

Non-isothermal kinetic data

T (°C)	α	T (°C)	α
335	0.07	363	0.55
342	0.13	365	0.62
344	0.15	371	0.77
347	0.18	374	0.84
353	0.25	376	0.88
358	0.36	378	0.93
360	0.46	380	0.96

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* The non significant values corresponding to the induction and the decay periods are not included.

TABLE 2

Non-isothermal kinetic results

$F(\alpha)$ [a]	Model	E_a (kcal mol^{-1})	r Correlation coefficient	S (e.u.)
Diffusion				
$D_1 = \alpha^2$	One-dimensional, parabolic law	83	0.9764	5.4
$D_2 = (1 - \alpha)\ln(1 - \alpha) + \alpha$	Two-dimensional, cylindrical symmetry	91	0.9841	6.5
	Three-dimensional, spherical symmetry			
$D_3 = (1 - (1 - \alpha)^{1/3})^2$	Jander equation	103	0.9932	8.2
$D_4 = (1 - 2/3\alpha) - (1 - \alpha)^{2/3}$	Ginstling equation	95	0.9876	6.8
Nuclei growth				
$F_1 = \ln(1/1 - \alpha)$	Random nucleation	57	0.9977	1.5
$A_2 = \ln(1/1 - \alpha)^{1/2}$	Avrami equation	27	0.9977	−3.3
$A_3 = \ln(1/1 - \alpha)^{1/3}$	Avrami equation	17	0.9977	−4.9
Phase boundary				
$R_1 = \alpha$	One-dimensional, zero order	40	0.9764	−1.3
$R_2 = 1 - (1 - \alpha)^{1/2}$	Two-dimensional, one-half order	47	0.9895	−0.3
$R_3 = 1 - (1 - \alpha)^{1/3}$	Three-dimensional, two-thirds order	50	0.9932	0.1

[a] Sharp's notation [10].

[6]. We have used the Šatava's integral method making the integration numerically [6].

The logarithmic form of the integrated expression of the general kinetic equation can be written as

$$\log F(\alpha) - \log P(x) = \log(ZE/aR)$$

where a is the heating rate, Z and E are the kinetic parameters from the Arrhenius law, $F(\alpha)$ is the function (T-dependent) which characterizes the model and $P(x)$ arises from the integration procedure [7].

The data treatment has been performed using a HP-83 computer by means of a calculation program designed ad hoc. This program (1) calculates the α values, (2) calculates the $F(\alpha)$ values for each model, (3) performs a least square fitting of the log $F(\alpha)$ vs. T^{-1} straight line and (4) calculates, for each model, the activation energy and the pre-exponential factor which minimize the dispersion of the function $B(\alpha) = \log F(\alpha) - \log P(x) =$ constant *.

It may be assumed that the model leading to the best fit would indicate the more likely mechanism.

The results from this analysis are listed in Table 2.

As can readily be seen, it is difficult to extract unambiguous conclusions taking only into account the reported r values. Thus, as it has been already stated [8], in absence of additional information, the procedure is unable to differentiate between diffusion and phase-boundary mechanisms. On the other hand, there is not a great difference among the r values corresponding to the D_3 and R_3 models and those obtained for the random nucleation models.

While, at this point, to appeal to isothermal procedures might appear as the only alternative, we will return to this question later.

Isothermal kinetics

The avoid the troubles mentioned above, isothermal thermogravimetry has been applied to the analysis of the reaction we are dealing with.

The dependence of the fraction of reaction (α) on the temperature (T) is shown in the Fig. 1 as a function of the time (t).

The kinetic data (couples α vs. t) from the isothermal TG curve obtained at 346°C have been used to assay the models proposed by Hulbert [3] (see Table 3). The result of this test is shown in Fig. 2. As can be observed, at this temperature, both nuclei growth and phase-boundary mechanism types are easily rejectable because the non-linearity of the respective $F(\alpha)$ vs. t functions. This way, a diffusion mechanism must be assumed. A survey of the plots in the Fig. 2 makes it evident that the experimental data fit equally

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* The values of $P(x)$ are also calculated in the program run.

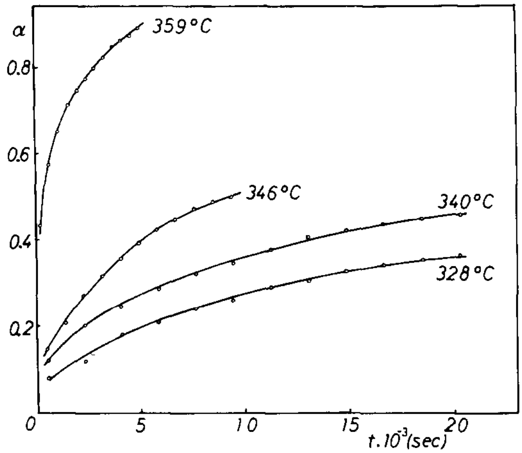

Fig. 1. Isothermal reaction curves (fraction of reaction as a *t* function at several temperatures).

TABLE 3

Isothermal kinetic models studied

Model	Equation	Mechanism type
Diffusion		
F_1	$K_1t=[1-(1-\alpha)^{1/3}]^2$	Jander (J)
F_2	$K_2t=\left[\left(\frac{1}{1-\alpha}\right)^{1/3}-1\right]^2$	Zhuravlev–Lesokhin–Tempel'man (ZLT)
F_3	$K_3t=[(1-2/3\alpha)-(1-\alpha)]^{2/3}$	Ginstling–Brounshtein (GB)
F_4	$K_4t=\ln[6/\pi^2(1-\alpha)]$	Dunwald–Wagner (DW)
Phase boundary		
F_5	$K_5t=1-(1-\alpha)^{1/2}$	Two-dimensional
F_6	$K_6t=1-(1-\alpha)^{1/3}$	Three-dimensional
Nuclei growth		
F_7 [a]	$K_7t^m=\ln(1-\alpha)^{-1}$	Nucleation

[a] Assayed for $m=0.51$. This m value came from the Handcock procedure [9].

well to Jander (F_1) and Ginstling–Brounsthein (F_3) models. To elucidate this indefiniteness requires an additional criterion. The constancy of K (rate constant) with time provides an efficient one * (Table 4).

As can be seen, whereas the K_J values display a monotonous increasing tendency with the time, those of K_{GB} show the typical dispersion of an experimental horizontal straight line.

Based on the foregoing discussion, it can be stated that the reaction between BaO_2 and $FeSO_4$ occurs, at 346°C, through a diffusion mechanism formally described by means of the GB model.

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* The Handcock and Sharp's procedure [9] neither led to conclusive results.

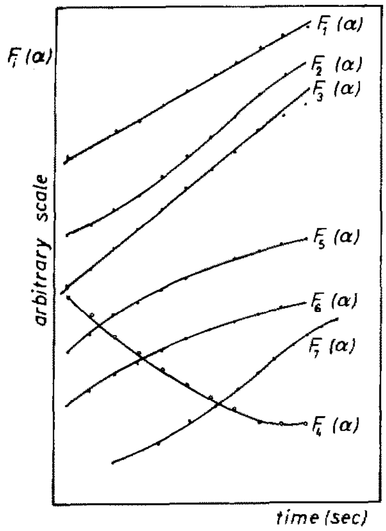

Fig. 2. Analysis of the studied models (F(α) vs. t functions).

The validity of this model for the entire working range of temperatures can now easily be checked. From the slopes of the $F_3(\alpha)$ vs. t straight lines obtained, the following rate constant (K_{GB}) values (s^{-1}) can be infered: $K_{GB}^{328} = 7.42 \times 10^{-7}$; $K_{GB}^{340} = 1.44 \times 10^{-6}$; $K_{GB}^{346} = 4.00 \times 10^{-6}$ and $K_{GB}^{359} = 2.49 \times 10^{-5}$.

Kinetic parameters

The above rate constant (K_{GB}^{T}) values fit well to a straight line (log K vs. T^{-1}) according to the Arrhenius law. Calculations based on the least-squares analysis yield the activation energy $E_a = 86.5$ kcal mol^{-1} and the pre-exponential factor $Z = 2.1 \times 10^{25}$ s^{-1}.

TABLE 4

Variation of rate constants values with time

Time (s)	$K_J \times 10^6$	$K_{GB} \times 10^6$
2250	4.80	4.18
3150	4.39	4.04
4050	4.59	4.17
4950	4.60	4.21
5850	4.71	4.19
6750	4.70	4.14
7650	4.78	4.17
8550	4.68	4.05

These last values can be now compared with those obtained when non-isothermal procedures were applied (see Table 2). The kinetic parameters then calculated can be clearly classified into three groups corresponding to the three possible formal mechanism types. Obviously, the value set from the diffusion models resembles most closely that provided by the isothermal experiments.

This way, a first conclusion must be emphasized: in the case of a reaction such as that considered here *, the mechanism type could be established from a single non-isothermal TG experience if a previous reliable evaluation of the kinetic parameters were available. Given that there are mathematical approaches allowing one to make that evaluation from a single non-isothermal TG curve [4], the requirement of one additional isothermal experiment (as proposed by Criado and Morales [8]) may be not indispensable.

Thus, we have applied the Abou-Shaaban and Simonelli's method [4] to the same TG curve used to perform the non-isothermal analysis. The values now calculated, $E_a = 76.4$ kcal mol^{-1} and $Z = 1.7 \times 10^{23}$ would have rendered possible the assignation of the more likely mechanism **.

On the other hand, the above results show that the use of the "best" r, (Table 2) as criterion to establish the "best" model is highly unsuitable. Thus, not only the actual mechanism is not a nucleation one but also, among the diffusion models, that leading to the best r is not that demonstrated by the isothermal analysis.

CONCLUSIONS

According to the objectives indicated above, it can be stated that the reaction between BaO_2 and $FeSO_4$ yielding $BaFeO_3$ proceeds formally through a diffusion mechanism. The process is adequately described by the Ginstling–Brounsthein three-dimensional diffusion model. Although the elucidation of the true mechanism giving a microscopic picture of the reaction exceeds the limits of the present paper, it may be interesting to offer some suggestion consistent with the chemical and mechanistic information now available. Then, it may be assumed that the counter diffusion of the Fe^{2+} and one half of the bulky Ba^{2+} cations is the rate controlling step.

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* Reaction that, as has been previously stated [5], occurs in a single stage.

** It has long been known that the values of the kinetic parameters determined by means of non-isothermal procedures are strongly influenced by the experimental variables (hence the denomination "procedural" values [2]). Accordingly, only the relative order of magnitude might be significant but the fact that both treatments of the non-isothermal data have been performed from the same TG curve would enable us to make the choice of mechanism type. Notwithstanding this, as it happens, in the present case, to go further on and try to pick out the formal model would probably lead to erroneous conclusions.

Really, it is not striking that this process is slower than the subsequent structural modifications. Thus, to replace Fe^{2+} by Ba^{2+} in the packing of sulphate groups (which is a thermodynamically favoured process) only would imply a rearrangement of the tetrahedral SO_4^{2-} units [11]. At the same time, the O_2 evolution associated with the electronic transference from Fe^{2+} to O_2^{2-} would leave an open structure in which the change of the coordination polyhedron around the remaining Ba^{2+} (required by the hexacoordination of the Fe(IV) in the perovskite type structure of the $BaFeO_3$) could be facilitated.

On the other hand, dealing with the feasibility of the non-isothermal procedures, our results permit us to conclude that, at least in the case of reactions occurring in a single stage (as is the studied here), it would be possible to elucidate the formal kinetics from the data provided by a sole TG curve. Nevertheless, in order to identify the definite kinetic model, an additional isothermal experiment would be required.

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