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Investigation of the impurity effect of zinc of the decomposition reaction of lead oxalate by isothermal TG. Experiments in flowing nitrogen

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Abstract

The decomposition of lead oxalate under flowing nitrogen has been investigated by using isothermal TG. The reaction is shown to follow the Avrami–Erofeev $A_2(\alpha)$ mechanism with $n = 2$. The activation energy was determined as 119.5 ± 7.0 kJ mol^{-1}. Doping the lead oxalate with zinc at the 1% level did not affect the reaction mechanism but was found to increase the activation energy to 137 ± 5.0 kJ mol^{-1}. This can possibly be explained on the basis that the zinc restricts the formation of cracks along which the decomposition is favoured.

INTRODUCTION

The thermal decomposition of lead oxalate has long been of interest. The dependence of the CO_2/CO ratio and the nature of the "lead oxide" residue on the experimental conditions is still in need of clarification. Bircumshaw and Harris [1, 2] carried out extensive studies of the decomposition of lead oxalate in vacuo, analysing the CO/CO_2 ratio as well as the residues obtained under various conditions. They determined a value of 36 kcal mol^{-1} (151 kJ mol^{-1}) for the activation energy of the reaction. Morsi [3] studied the decomposition in air and reported that, below 60% decomposition, the reaction obeyed the Avrami–Erofeev equation with an activation energy of 34.3 kcal mol^{-1} (144 kJ mol^{-1}). Over the 60–95% decomposition range, a unimolecular reaction occurred, the activation energy being 33.4 kcal mol^{-1} (140 kJ mol^{-1}).

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In 1957, Yankwich and Copeland [4] used a mass spectrometric technique to study the composition and isotopic constitution of the gaseous products. The temperature dependence of the CO_2/CO ratio and the carbon isotope distribution ratio were considered in terms of simple models. A study of the decomposition of lead oxalate before and after γ-irradiation has been reported by Herley and Prout [5]. Their results indicated that γ-irradiation led to a reduction in the activation energy to 76 kcal mol^{-1} (318 kJ mol^{-1}).

We have undertaken a study of the decomposition of lead oxalate using a variety of thermal analysis/evolved gas analysis techniques and a range of different sample treatments. This paper reports the isothermal decomposition under flowing nitrogen both of lead oxalate and of lead oxalate doped with 1% of zinc.

EXPERIMENTAL

Thermogravimetry

Thermogravimetric studies were carried out using a Stanton–Redcroft TG-750 thermobalance through which nitrogen flowed at 50 ml min^{-1}. Isothermal experiments were conducted at 611.5, 658.5, 665.0, 673.5 and 706.6 K.

Lead oxalate preparation and treatments

The lead oxalate sample was prepared in the following way. Ammonium oxalate was first prepared by adding ammonium hydroxide solution to 0.2 N oxalic acid (AnalaR grade) until the solution commenced to show the alkali blue response when tested with litmus paper. The solution thus obtained, was then dropped slowly into 0.2 N lead nitrate (Merck reagent grade), which was stirred on a magnetic mixer. Lead oxalate precipitated from solution. Doped samples were similarly produced except that zinc nitrate, at the 1% level, was included in the lead nitrate solution.

The lead oxalate precipitate was filtered off, well washed with distilled water and then dried in an oven at 80°C for several days. It was then sieved and stored in plastic containers. Particles in the 140–180 mesh range were used for subsequent thermogravimetric studies.

RESULTS

Lead oxalate sample

The experimental sample weight vs. time traces were converted to α, t data, where α is the fraction decomposed and t is the reaction time, in the usual way. These raw α, t data were then recalculated on a reduced time basis $t/t_{0.5}$, as proposed by Sharp [6]. The data are collated in Table 1.

TABLE 1

Calculated data for lead oxalate (140–180 mesh)

	Theoretical		Experimental				
			Temperature (K)/Reaction $t_{0.5}$ (s)				
	$A_2(\alpha)$	$A_3(\alpha)$	611.5 2155	658.5 182	665 171	673.5 125	706.6 42
α	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$
0.1	0.390	0.533	0.377	0.330	0.340	0.337	0.318
0.2	0.567	0.685	0.517	0.510	0.533	0.568	0.490
0.3	0.717	0.801	0.675	0.679	0.703	0.742	0.651
0.4	0.858	0.903	0.823	0.876	0.845	0.878	0.818
0.5	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.6	1.150	1.097	1.159	1.148	1.170	1.178	1.177
0.7	1.318	1.198	1.363	1.346	1.357	9.365	1.389
0.8	1.524	1.322	1.613	1.549	1.604	1.598	1.668
0.9	1.822	1.492	1.974				
α	$[-\ln(1-\alpha)]^{1/2}$	$\ln[-\ln(1-\alpha)]$	t	t	t	t	t
0.1	0.325	−2.250	726	60	58	42	13
0.2	0.472	−1.555	1113	93	91	71	21
0.3	0.597	−1.031	1454	124	121	93	27
0.4	0.715	−0.672	1772	160	145	110	34
0.5	0.833	−0.367	2155	182	171	125	42
0.6	0.957	−0.087	2496	209	201	148	49
0.7	1.097	0.186	2935	245	233	171	58
0.8	1.269	0.476	3473	282	275	200	70
0.9	1.517	0.834	4251				
Calculated data from $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ plots							
Slope n			1.75	1.75	1.77	1.80	1.68
Correlation coefficient			0.99	0.99	1.00	0.99	0.99

Rate constant (k) values as the slope of $[-\ln(1-\alpha]^{1/2}$ versus t plots

Temp (K)	k (s^{-1})
611.5	7.01×10^{-4}
658.5	42.13×10^{-4}
665.0	43.10×10^{-4}
673.5	60.78×10^{-4}
706.6	160.70×10^{-4}

Figure 1 shows the α against $t/t_{0.5}$ plot for the data obtained at 611.5 K, together with the plots for the Avrami–Erofeev equation [7, 8] for $n = 3$, the $A_3(\alpha)$ mechanism and $n = 2$, the $A_2(\alpha)$ mechanism. Similar plots were obtained at the four other temperatures investigated. Although neither mechanism gives a perfect fit to the experimental points, the $A_2(\alpha)$ mechanism is a much closer fit than is the $A_3(\alpha)$ one.

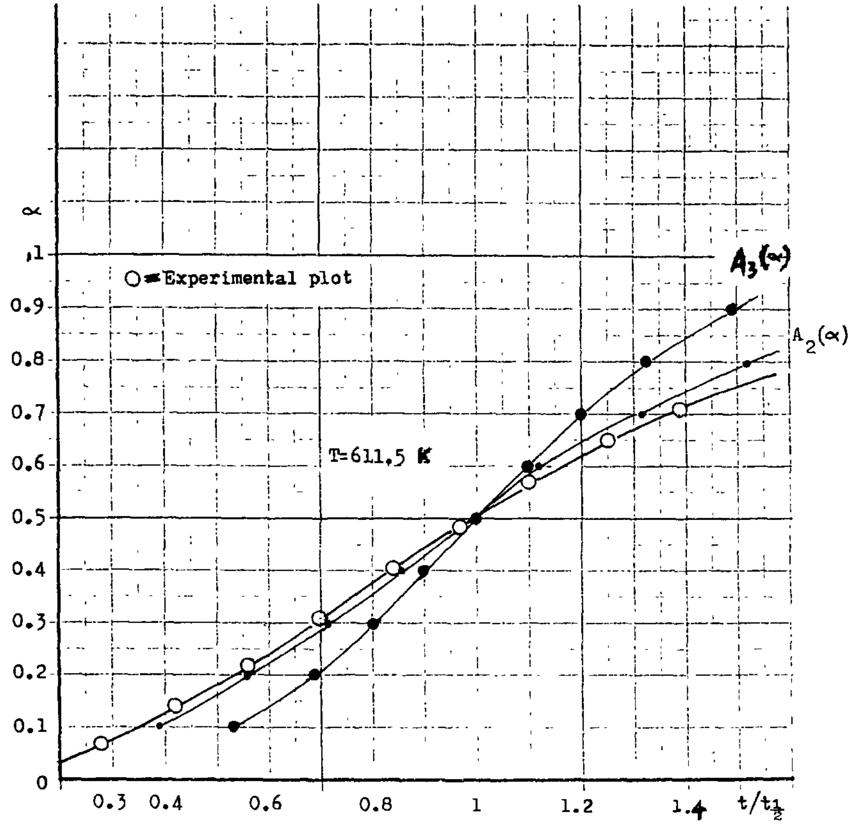

Fig. 1. Reduced time plot for lead oxalate data: ○, experimental points; •, theoretical $A_2(\alpha)$ points; ●, theoretical $A_3(\alpha)$ points.

A log–log analysis was also applied to the data to obtain an alternative evaluation of *n*, the reaction order. The data used is also collated in Table 1. Plots of $\ln(-\ln(1-\alpha))$ against *t* were linear with a good fit to the experimental data. The gradient of such plots yields a value for *n*, the exponent in the Avrami–Erofeev equation. A standard computer program was used to calculate the gradient and correlation coefficient for the best straight line fit to the data. As shown in Table 1, the values obtained for *n* lie in the range 1.75 ± 0.07, with very high correlation. This again favours the $A_2(\alpha)$ mechanism. Accepting that the data indicates that the $A_2(\alpha)$ mechanism is operating under the conditions of these experiments, then the Avrami–Erofeev equation for this mechanism

$$-\ln(1-\alpha)^{1/2} = kt$$

can be used to evaluate the rate constant *k* at the five temperatures studied. The values obtained are presented in Table 1, and were used to calculate the activation energy via the Arrhenius equation in the usual way. A value of 119.5 ± 7.0 kJ mol^{-1} was obtained.

1% *Zn-doped lead oxalate*

The thermogravimetric study of the doped lead oxalate sample was conducted as described previously for the non-doped sample. The five temperatures investigated were 614.6, 633.0, 655.8, 659.6 and 662.7 K. The experimental data were treated as before and are collated in Table 2. The typical α against $t/t_{0.5}$ plots presented in Fig. 2 show that, in the case

TABLE 2

Calculated data for 1% Zn-doped lead oxalate (140–180 mesh)

	Theoretical		Experimental				
			Temperature (K)/Reaction $t_{0.5}$ (s)				
	$A_2(\alpha)$	$A_3(\alpha)$	614.6 1360	633 623	655.8 261	659.6 204	662.7 157
α	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$	$t/t_{0.5}$
0.1	0.390	0.533	0.385	0.407	0.382	0.371	0.229
0.2	0.567	0.685	0.563	0.575	0.565	0.544	0.462
0.3	0.717	0.801	0.714	0.718	0.720	0.705	0.642
0.4	0.858	0.903	0.856	0.853	0.867	0.851	0.822
0.5	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.6	0.150	1.097	1.152	1.151	1.158	1.164	1.190
0.7	1.318	1.198	1.334	1.322	1.325	1.350	1.375
0.8	1.524	1.322	1.559	1.534	1.514	1.658	1.656
0.9	1.822	1.492	1.878	1.822	1.786	1.895	
α	$[-\ln(1-\alpha)]^{1/2}$	$\ln[-\ln(1-\alpha)]$	t	t	t	t	t
0.1	0.325	−2.250	533	254	99	76	39
0.2	0.472	−1.155	765	358	147	111	72
0.3	0.597	−1.031	971	447	187	144	101
0.4	0.715	−0.672	1164	531	226	174	129
0.5	0.833	−0.367	1360	623	261	204	157
0.6	0.957	−0.087	1566	717	301	238	186
0.7	1.097	0.186	1814	824	352	276	215
0.8	1.269	0.476	2120	956	394	339	260
0.9	1.517	0.834	2553	1135	465	387	

Rate constant (k) values as the slope of $[-\ln(1-\alpha)]^{1/2}$ versus t plots

Temp (K)	k (s^{-1})
614.6	5.88×10^{-4}
633.0	13.36×10^{-4}
655.8	32.26×10^{-4}
659.6	36.88×10^{-4}
662.7	42.28×10^{-4}

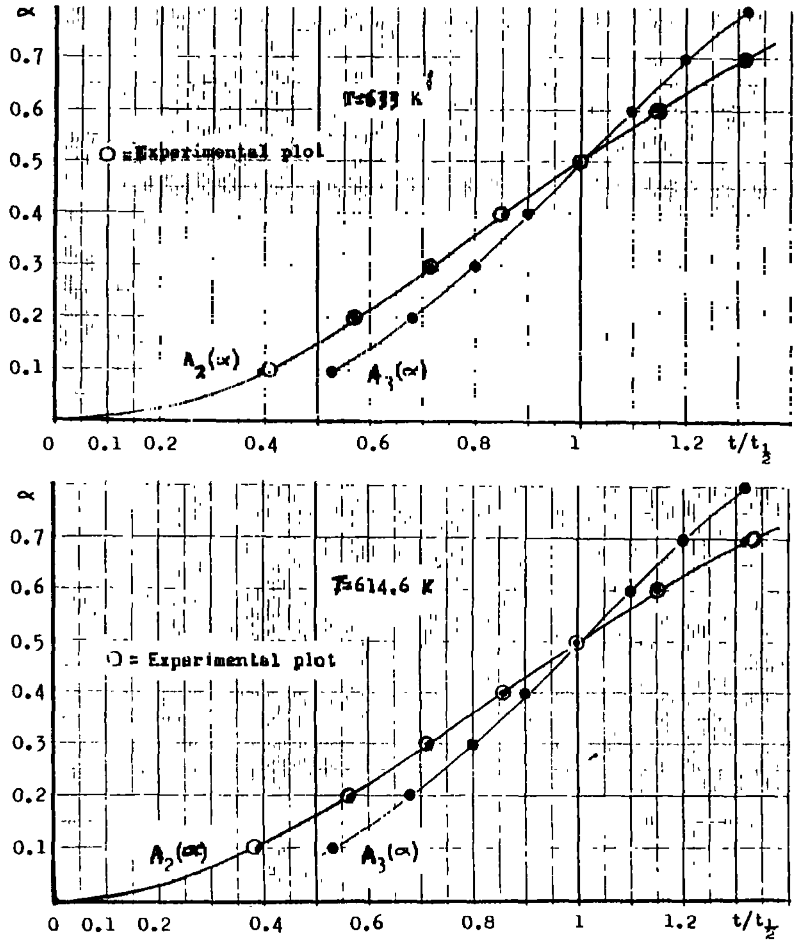

Fig. 2. Reduced time plot for 1% Zn-doped lead oxalate data: ○, experimental points; •, theoretical $A_2(\alpha)$ points; ●, theoretical $A_3(\alpha)$ points.

of the doped sample, the A_2 experimental points are a very good fit to the $A_2(\alpha)$ curve. Thus the rate constants at each temperature could be evaluated from the Avrami–Erofeev equation for $n = 2$. A value of $137.5 \pm 5.0\ \text{kJ mol}^{-1}$ was calculated for the activation energy from the temperature dependence of the rate constant.

DISCUSSION

The value of $119.5 \pm 7.0\ \text{kJ mol}^{-1}$ obtained for the activation energy for lead oxalate decomposition in nitrogen is somewhat lower than the values of $151\ \text{kJ mol}^{-1}$ obtained in vacuo [1, 2] and $144\ \text{kJ mol}^{-1}$ obtained in air [3]. However, the data obtained do support the Morsi conclusion that the decomposition is best described by the Avrami–Erofeev mechanism

$A_2(\alpha)$ with $n = 2$. Since the reaction concerned involves the decomposition of solid particles, then the $n = 2$ result is best explained in terms of a mechanism involving random nucleation followed by two dimensional growth. This is compatible with the kinetic evidence of Bircumshaw and Harris [2], which conformed to predictions based on a model in which branching starts at nuclei and spreads through branching chains along paths of lateral strain; the strain is relieved by the formation of Smekal cracks along, which the decomposition is favoured. The other detailed consideration of the lead oxalate decomposition mechanism is that of Yankwich and Copeland [4]. This was based on a mass spectrometric study of isotope effects in the CO_2/CO ratio of the gaseous products. Satisfactory agreement with their experimental data was obtained for a model based on competition between oxygen abstraction and C–C bond rupture. This was based primarily on the Bigeleisen–Wolfsberg treatment of three-centre reactions; the model for the activated complex includes a lead atom. Although the current results do not facilitate such detailed consideration of the decomposition at the molecular level, they do confirm that decomposition is initiated at random nuclei and spreads from there.

The other interesting result from the current work is that the introduction of 1% of Zn as an impurity into the lead oxalate grains raises the activation energy by some $18\ \mathrm{kJ\ mol^{-1}}$. The mechanism remains the same but the data much more clearly fits the $A_2(\alpha)$ mechanism than did that for the non-doped samples. Although the increase is small, it is nonetheless real. A possible explanation could be that the presence of the zinc oxalate within the lead oxalate crystal lattice restricts the formation of the Smekal cracks along which decomposition is favoured [2].

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REFERENCES

1 L.L. Bircumshaw and I. Harris, J. Chem. Soc. (1939) 1637.
2 L.L. Bircumshaw and I. Harris, J. Chem. Soc. (1948) 1898.
3 S.E. Morsi, J. Chem. U.A.R., 3 (1970) 113.
4 P.E. Yankwich and J.L. Copeland, J. Am. Chem. Soc., 79 (1957) 2081.
5 P.J. Herley and E.G. Prout, J. Inorg, Nucl. Chem., 16 (1960) 16.
6 J.H. Sharp, G.W. Brindley and B.N. Narahaki Archer, J. Am. Ceram. Soc., 49 (1966) 379.
7 M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212.
8 B.V. Erofeev, Dokl. Akad. Nauk SSSR, 52 (1946) 511.