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INFLUENCE OF SELECTED METAL OXIDES ON THE OXIDATION KINETICS OF GRAPHITE

S. SAMPATH, N.K. KULKARNI and D.M. CHACKRABURTTY

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

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ABSTRACT

The thermal decomposition of graphite in air was studied in detail by thermogravimetry in the presence of varying concentrations of U_3O_8, CeO_2 and ThO_2. The decomposition was found to follow first-order kinetics with a significant decrease in decomposition temperatures and activation energies, E, due to presence of the oxides. There was a decrease in log A, associated with a decrease in E, indicating the kinetic compensation effect. One of the possible mechanisms for catalysis, namely localized reduction of the oxide by graphite followed by reoxidation of the lower oxide by air, is not supported by the results obtained.

INTRODUCTION

Gas reactions of graphite have been studied in detail and the majority of results show that the graphite–oxygen reaction follows first-order kinetics with activation energies in the range 48–58 kcal mol^{-1} [1–3]. Isothermal methods have been used in deriving kinetic data and impurities have been found to catalyse the graphite oxidation process with a consequent reduction in activation energies. Two mechanisms have been proposed for the behaviour of metal oxides as catalysts in the oxidation of carbon surfaces by air or oxygen:

(1) impurities interact with the π electrons of the basal planes in carbon thus altering the bond order of the surface carbon;

(2) an oxidation–reduction cycle in which carbon is oxidised by metal oxide which is itself reduced to a lower oxide. Reoxidation to a higher oxide is effected by the main air stream. This mechanism presupposes the existence of at least two stable oxides of different valencies for an oxide to act as catalyst in the graphite decomposition.

To get an insight into this problem, there is a need to study the thermal behaviour of carbon, in presence of excess oxides of metals of otherwise similar nature but with multiple valence states. With this view, the kinetics of thermal decomposition of graphite in air were studied in detail in the presence of varying amounts of U_3O_8, cerium dioxide, ThO_2 and alumina.

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EXPERIMENTAL

Mixtures of graphite (Spec. Pure) and metal oxides (U_3O_8, CeO_2, ThO_2) were prepared in different concentrations by intimate mixing of appropriate amounts of graphite and the oxide in an agate mortar with a few drops of alcohol, and then drying under an IR lamp. Thermogravimetry (TG) and differential thermal analysis (DTA) of the samples were carried out using a Mettler thermoanalyser in air at a constant flowing rate of 100 ml min^{-1} and uniform heating rate of 4°C min^{-1}. Platinum crucibles of 8 mm diameter and 11 mm length were used in all the experiments. All the oxides were heated to 800°C in air prior to mixing with graphite to drive off traces of moisture.

RESULTS AND DISCUSSION

From the TG curves obtained it was observed that the decomposition temperatures of graphite were considerably decreased in the presence of U_3O_8. Values of α at varying temperatures were calculated from the ratio of the weight loss observed at temperature T, to the total weight loss. $\text{Log}[-\log(1-\alpha)]/T^2$ values were plotted against $1/T$ and are shown in Fig. 1. First-order plots based on the method of Coats and Redfern [4] were obtained. The X–Y plots shown in Fig. 1 were obtained by a least-squares

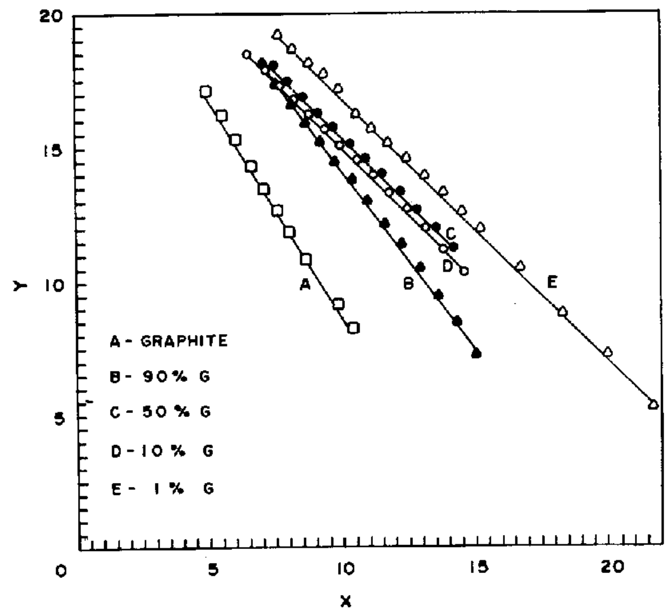

Fig. 1. First-order plots for graphite decomposition in the presence of U_3O_8.

TABLE 1

Kinetic data on the catalytic decomposition of graphite (G) in the presence of U_3O_8

%G	T_d (°C)	Range of α linearity	Slope	C	E (kcal mol^{-1})	log A
100	640	0.1–0.9	1.196×10^4	+4.065	54.8	9.2
90	560	0.1–0.9	9.45×10^3	+2.86	43.5	7.8
50	530	0.2–0.9	7.19×10^3	+0.765	33.1	5.6
10	530	0.2–0.9	7.16×10^3	+0.690	32.9	5.5
1	490	0.1–0.9	7.0×10^3	+0.790	32.2	5.6

fit and the graphs were plotted on the Calcomp plotter with $Y=[Y^*+8.6]\times 7$, $Y^*=\log[-\log(1-\alpha)]/T^2$; $X=[X^*\times 1000-8]\times 5$, $X^*=1/T$. The plots were found to be linear in the α-range from 0.3 to 0.9, indicating first-order kinetics, and activation energies were calculated from the slopes. Table 1 gives T_d values (the temperature at which the decomposition of graphite becomes measurable in TG) for different concentrations of U_3O_8, the range of α in which first-order plots are linear, activation energies, E, and log A values. There is a decrease in the decomposition temperatures of graphite due to the presence of U_3O_8. Pure graphite decomposes above 600°C, whereas the presence of U_3O_8 reduces the decomposition temperatures to 500°C and below.

It is also seen from Table 1 that there is a decrease in the activation energies for the oxidation of graphite due to the presence of U_3O_8, thus

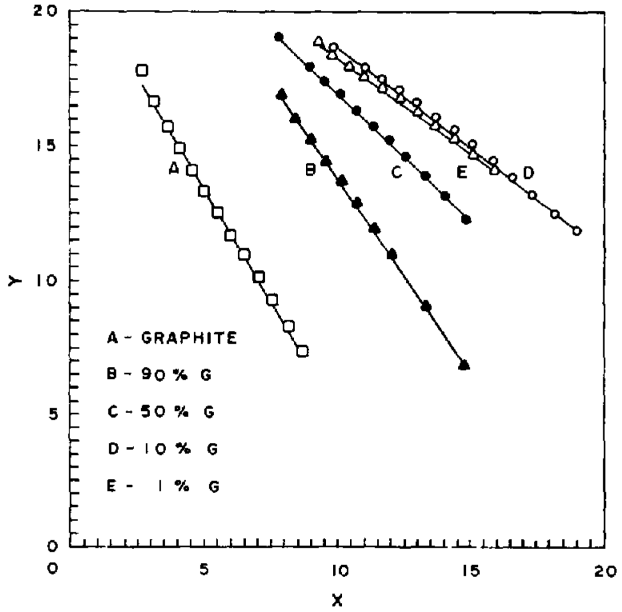

Fig. 2. First-order plots for graphite decomposition in the presence of CeO_2.

TABLE 2

Kinetic data on the catalytic decomposition of graphite (G) in the presence of CeO_2

%G	T_d (°C)	Range of α linearity	Slope	C	E (kcal mol^{-1})	log A
100	640	0.1–0.9	1.196×10^4	+4.065	54.8	9.2
90	570	0.1–0.9	1.03×10^4	+3.662	47.4	8.6
50	540	0.2–0.9	6.74×10^3	+0.54	31.0	5.3
10	450	0.2–0.9	5.41×10^3	−0.526	24.9	4.3
1	450	0.3–0.9	5.06×10^3	−0.949	23.3	3.8

suggesting the probable catalytic effect of U_3O_8 in graphite decomposition. The activation energy data for pure graphite are in agreement with the literature data obtained by isothermal method [1–3].

Thermogravimetric curves of graphite in the presence of CeO_2 were similar to those of graphite–U_3O_8. First-order plots for the decomposition are given in Fig. 2. Table 2 gives concentrations of graphite in CeO_2, T_d values, range of α in which the first-order plots are linear, E and log A values. In general, it is observed that at graphite concentrations of 10% and below, the activation energy values were similar, indicating that a further increase in the concentrations of U_3O_8 or CeO_2 did not have any additional effect on the oxidation of graphite.

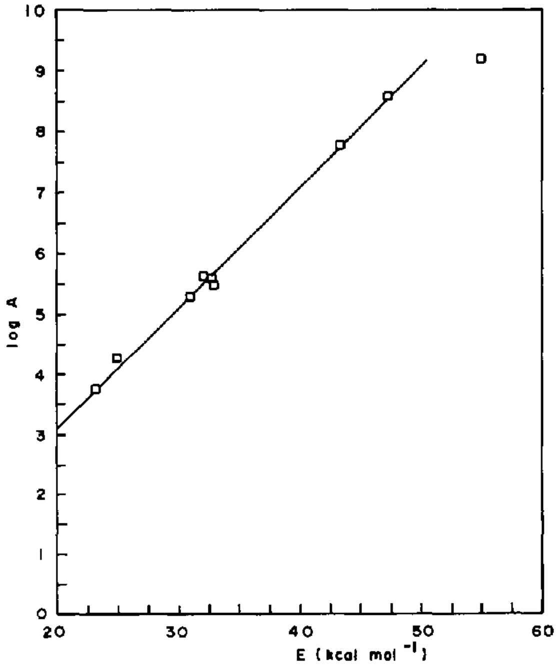

Fig. 3. Log A vs. E plot for the catalytic decomposition of graphite.

Tables 1 and 2 show that a decrease in log A values is associated with a decrease in E. The plot of log A vs. E shown in Fig. 3 gives a linear plot indicating the kinetic compensation effect. This has also been reported earlier on catalysed decompositions of graphite [5]. The average isokinetic temperature $\bar{T}_s$, i.e., the temperature at which reaction rates are equal for catalysed and uncatalysed reactions, was obtained from the slope of the log A vs. E plot using the relationship $\ln A = \ln \bar{k}_0 + E/R\bar{T}_s$; $\bar{T}_s$ was thus found to be 1087 K. Since most of the graphite decompositions in our studies are completed below 1087 K, the activation energy observed in all cases is sum of both catalysed and uncatalysed decompositions of graphite in our experiments.

The method of Satava and Skvara [6] for obtaining kinetic data from non-isothermal TG involves a comparison of log f(α) vs. T plots with log p(x) vs. T plots, which we have earlier used in our studies on the U–Pu–O system and which was found to agree very well with isothermal data [7]. This was also tried in the catalytic decomposition of graphite to corroborate our data. The f(α) used was $-\ln(1-\alpha)$, applicable for first-order kinetics. Figures 4 and 5 give curve fits for pure graphite and the catalysed decom-

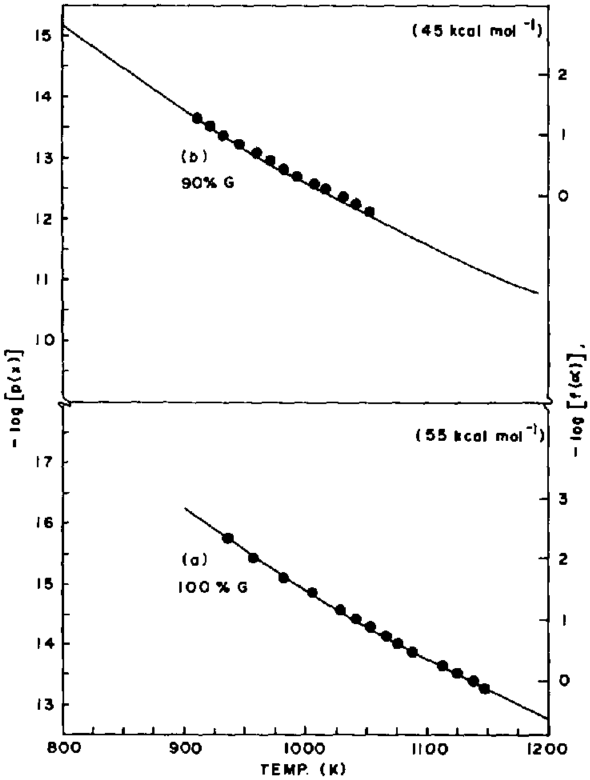

Fig. 4. Thermal decomposition of graphite catalysed by U_3O_8. Non-isothermal kinetic curve fit.

position of graphite by U_3O_8. The curves show log p(x) vs. T plots for the E values specified and the shaded points show log f(α) vs. T values obtained experimentally. Figure 6 gives curve fits for the CeO_2-catalysed decomposition of graphite for different concentrations of CeO_2. Table 3 gives a comparison of E and log A values obtained by (A) the method of Coats and Redfern and (B) the method of Satava and Skvara. There is a reasonable agreement between the data obtained by the two methods.

Two probable mechanisms have been proposed for the catalytic decomposition of graphite by metal oxides: (1) impurities interact with the π electrons of the basal planes in carbon; (2) an oxidation–reduction cycle in which carbon is oxidised by metal oxide which is itself reduced to a lower oxide. Reoxidation to a higher oxide is effected by the main air stream. At present there is not conclusive evidence to support either of these mechanisms. If the latter mechanism is assumed to operate in the case of catalysis by U_3O_8 then we have the two reactions

$$U_3O_8 + C \rightarrow 3UO_2 + CO_2 \qquad \text{(I)}$$

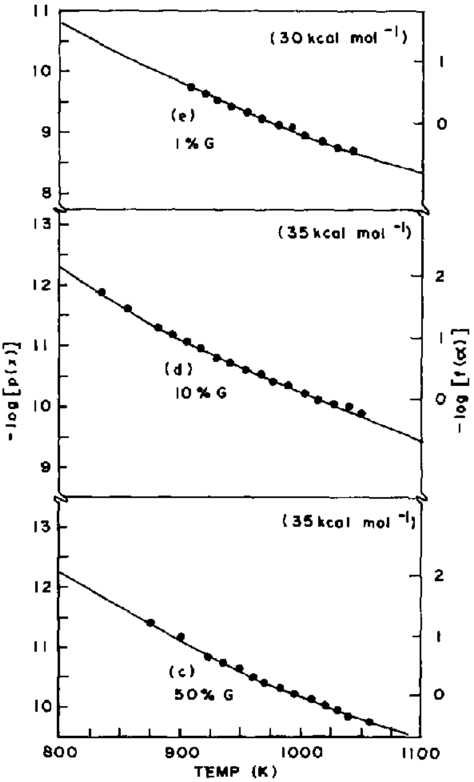

Fig. 5. Thermal decomposition of graphite catalysed by U_3O_8. Non-isothermal kinetic curve fit.

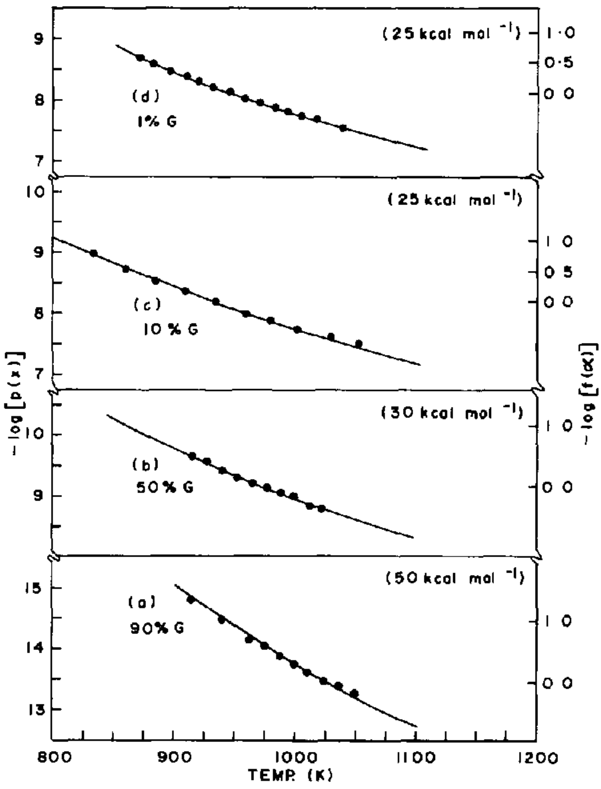

Fig. 6. Thermal decomposition of graphite catalysed by CeO_2. Non-isothermal kinetic curve fit.

TABLE 3

Comparison of E and log A values for the catalytic decomposition of graphite (G)

% G	Coats and Redfern		Satava and Skvara	
	E (kcal mol^{-1})	Log A	E (kcal mol^{-1})	Log A
A. Catalysis by U_3O_8				
100	54.8	9.2	55	9.5
90	43.5	7.8	45	8.5
50	33.1	5.6	35	6.4
10	32.9	5.5	35	6.4
1	32.2	5.6	30	5.5
B. Catalysis by CeO_2				
100	54.8	9.2	55	9.5
90	47.4	8.6	50	9.7
50	31.0	5.3	30	5.5
10	24.9	4.3	25	4.6
1	23.3	3.8	25	4.5

$$3UO_2 + O_2 \rightarrow U_3O_8 \tag{II}$$

For the catalysis of CeO_2 we have the two possible steps

$$4CeO_2 + C \rightarrow 2Ce_2O_3 + CO_2 \tag{I}$$

$$2Ce_2O_3 + O_2 \rightarrow 4CeO_2 \tag{II}$$

To probe into the possibilities of the existence of an oxidation–reduction cycle, mixtures of 10% graphite with U_3O_8 and CeO_2 were prepared and thermograms were run in argon. α vs. T plots are given in Fig. 7. For comparison, α vs. T plots of the same mixtures in air are also given. It is seen that U_3O_8 is reduced by graphite in the temperature range 500–800°C to UO_2 (as confirmed by the X-ray powder diffraction pattern of the products) and the rate of reduction is comparable to that of the catalytic decomposition of graphite by U_3O_8 in air. This is not true in the case of the reduction of CeO_2 by graphite, however, which is very slow above 550°C and reduction is incomplete even up to 1200°C.

In air the decomposition of graphite was also studied in the presence of ThO_2 and alumina, and α vs. T plots of the same are given in Fig. 7. It is seen that there is a considerable decrease in the decomposition temperatures of graphite in the presence of ThO_2, which is not observed in the presence of aluminium oxide. First-order plots gave E values of 27.6 and 37.7 kcal

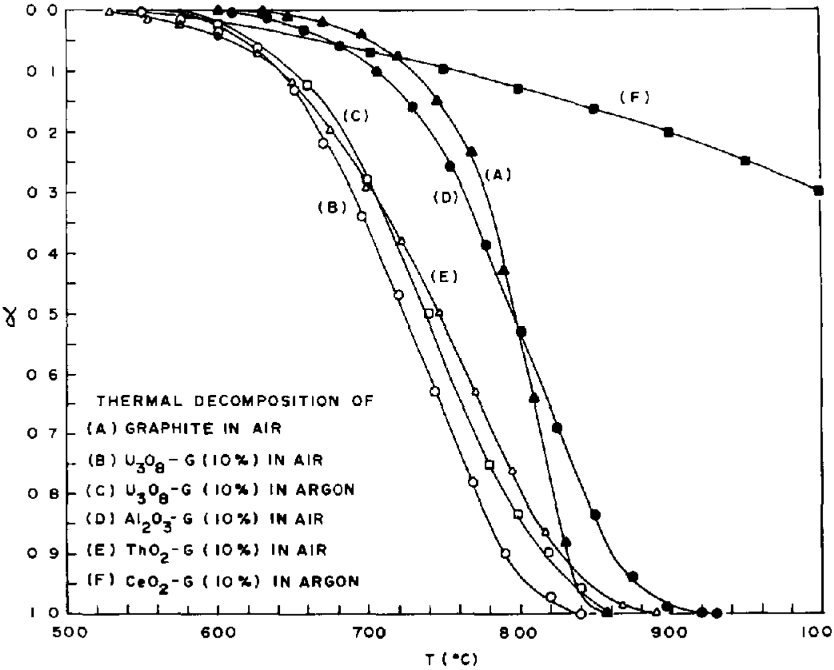

Fig. 7. α–T plots.

mol^{-1} for ThO_2-catalysed and alumina-catalysed decompositions, respectively.

Thorium dioxide, the only stable oxide of thorium, is also found to catalyse significantly. The decomposition of graphite in air and the extent of catalysis by ThO_2 are comparable to that by U_3O_8 and CeO_2 which are known to have stable lower valent oxides like UO_2, Ce_2O_3, etc. The reduction of CeO_2 by graphite in argon is very slow and not comparable to the decomposition rate of graphite. These results indicate that factors other than the reduction–oxidation cycle probably control the kinetics of graphite decomposition in these cases.

The following conclusions can be arrived from the results obtained.

(1) The decomposition of graphite in air is catalysed by such oxides as U_3O_8, CeO_2 and ThO_2. These decomposition follow first-order kinetics as shown by the non-isothermal methods of Coats and Redfern and Satava and Skvara, and there is good agreement in E values obtained by the two methods.

(2) The kinetic compensation effect is observed in catalytic decompositions of graphite by cerium oxide and U_3O_8.

(3) Catalysis of graphite decomposition by ThO_2 is similar to that by U_3O_8 and CeO_2. This indicates that a reduction–oxidation mechanism is not operative in these cases.

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