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Rates of Thermal Decomposition of Barium Carbonate–Carbon Mixtures

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The thermal decomposition of pure barium carbonate to form barium oxide and carbon dioxide requires relatively high temperatures; for example, at 1,030°C. the equilibrium partial pressure of carbon dioxide is only 2 mm. Hg (*3*). Unfortunately temperatures in excess of 1,030°C. tend to produce a dense, nonporous form of barium oxide. According to Lander (*3*), a barium carbonate–barium oxide eutectic exists at 1,030°C., and apparently above this temperature barium carbonate–barium oxide solutions form which continue to exist as solid solutions below the melting point. Therefore the thermal decomposition of barium carbonate is usually facilitated by the addition of carbon (*1, 2*). The carbon dioxide partial pressure becomes greatly reduced, since the following reaction proceeds far to the right:

$$C + CO_2 \rightarrow 2CO \qquad (1)$$

The observed rate of the over-all reaction may therefore be affected by heat or mass transfer rates or by the kinetics of two separate reactions.

EXPERIMENTAL

Barium carbonate was mixed with one of several forms of carbon, and the mixture was pressed (at 27,000 lb./sq. in.) into a cylinder around a platinum, rhodium–in–platinum thermocouple. The cylinder was calcined in a constant-temperature furnace of special design, and the rate of reaction was determined by the rate of the evolution of gas. The apparatus and methods employed were substantially the same as those used previously for studying the decomposition of calcium carbonate (*6*). This earlier paper also discusses the accuracy of the experimental data.

Lieberson and Oster (*5*) found that the rate of reaction of barium carbonate and carbon mixtures was not greatly influenced by the amount of carbon used in excess of that stoichiometrically required for the over-all reaction:

$$BaCO_3 + C \rightarrow BaO + 2CO \qquad (2)$$

(The stoichiometric ratio is 6.085 g. carbon/100 g. barium carbonate.) However to decrease the possibility of the carbon content being a rate-controlling factor, and also to decrease the effect of imperfect mixing, a 50% excess of carbon over the stoichiometric quantity was used in each run beyond the first.

Since it was also desirable to carry out the reaction at temperatures below that of the barium carbonate–barium oxide eutectic (1,030°C. or 1,886°F.), vacuum conditions were required. A mechanical vacuum pump was used to exhaust the furnace, and a Cartesian Diver manostat reduced pressure fluctuations. The rate of the evolution of gas (which was almost 100% carbon monoxide) was measured with a capillary flow meter. The over-all degree of decomposition of the barium carbonate was determined by measuring the weight of the sample before and after reaction.

Mallinckrodt reagent-grade barium carbonate was used in all runs. The average particle diameter was found to be about 0.13 μ; the B.E.T. surface area (by nitrogen adsorption) was about 10 sq. m./g. The properties of the different types of carbon studied are outlined in Table 1. The components were mixed dry, then wet (with water), and then again dry after removing the water by evaporation. The most efficient mixing probably took place when the mass was a thick paste. However despite the considerable care devoted to obtaining good mixing the degree of mixing was not so high as desired. Small "islands" of white barium carbonate, up to approximately 0.15 mm. in diameter, were visible in the pressed samples. Nevertheless, the degree of mixing was apparently sufficient to give complete decomposition of the barium carbonate, if reaction conditions were favorable.

In all cases a 0.010-in.-diameter platinum, 10% rhodium-in-platinum thermo-

TABLE 1. PROPERTIES OF CARBON BLACKS AND GRAPHITES STUDIED

Carbon Blacks

Code name	Type	Surface area, sq. m./g., by B.E.T.-Nitrogen Method	Mean particle diameter, (μ)	Ash content, wt. %
Elftex 5	Furnace black	77	0.03	0.5
Elf 8	Channel black	100	0.03	0.1
Sterling FT	Thermal black	15.7	0.20	0.1
Same-after partial graphitization		12.7	0.20	0.1

Graphites

Code name	Minimum graphitic carbon content, wt. %	Maximum ash, wt. %	Particle size
Dixon 2	94	5	30% + 100 mesh 30% − 200 mesh
Microfyne	94	5	97% − 325 mesh

TABLE 2. EXPERIMENTAL RESULTS

Run	Type of carbon	Excess carbon %	Cylinder radius, cm.	Length, cm.	Density, Before Reaction g./cc.	Furnace temperature, °F.	Furnace pressure, mm. Hg.	Reaction time, hr.	Conversion, %	Internal temperature range*, °F.
1	Elftex 5	5	1.13	7.06	1.42	1,834 ± 4	192 ± 5	5.75	90.3	1,726 to 1,743
2	Elf 8	50	1.045	6.49	1.25	1,767 ± 6	74 ± 2	3.5	103.1	1,626 to 1,633
3	Elf 8	50	1.11	6.02	1.16	1,720 ± 10	51 ± 4	4.17	102.1	1,605 to 1,611
4	Elf 8	50	1.12	7.11	1.21	1,817 ± 10	115 ± 10	3.27	102.3	1,682 to 1,690
5	Graphite Dixon 2	50	1.05	6.34	1.33	1,823 ± 3	53 ± 9	2.0	65.4	1,760 to 1,815
6	Graphite Microfyne	50	1.02	6.33	1.29	1,826 ± 2	26.5 ± 4	2.0	87.6	1,720 to 1,821
7	Graphitized Sterling FT	50	1.11	5.66	1.35	1,821 ± 8	54 ± 4	3.60	99.4	1,721 to 1,821
8	Sterling FT	50	1.12	5.72	1.34	1,815 ± 4	101 ± 8	2.07	100.8	1,677 to 1,685

*Temperature range quoted excludes transient conditions at beginning and end of run. The time-temperature curves for runs 2, 3, 4, and 8 were similar in shape to those shown on Figure 1. Those for runs 5 and 6 resembled Figure 2. Run 7 was intermediate between the two types.

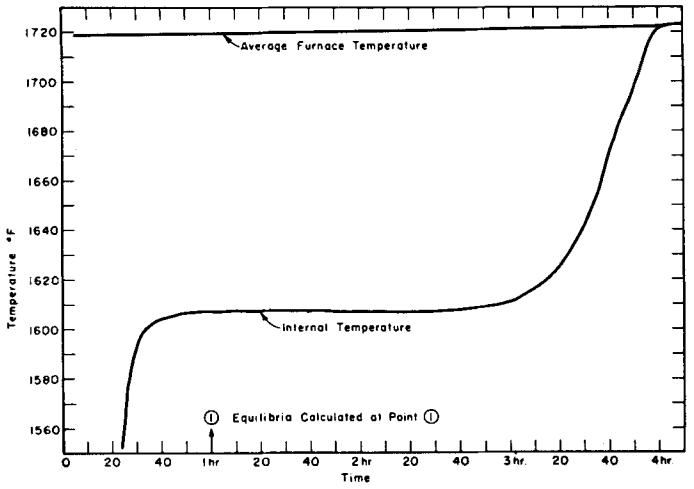

Fig. 1. Calcination of barium carbonate-carbon black mixture (run no. 3).

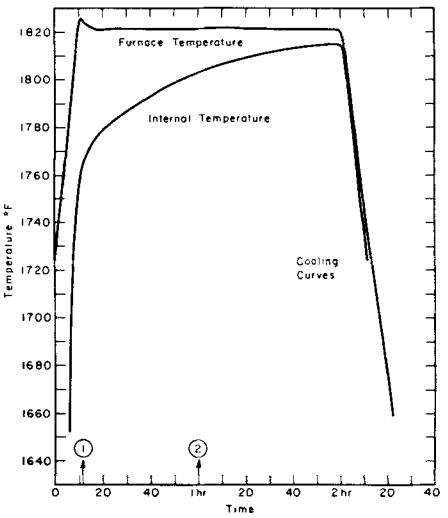

Fig. 2. Calcination of barium carbonate-graphite mixture (run no. 5). Equilibria calculated at points 1 and 2.

couple was embedded axially within the cylinder. Since carbon is a conductor, in all runs after run 2 the thermocouple was insulated with alundum cement baked on by resistance heating of the thermocouple. After coating, the resistance from the thermocouple to the carbon mixture exceeded 50 mohm. However judging from the data one concludes that this precaution was unnecessary here.

RESULTS

The experimental results are summarized in Table 2. Following are some general observations and explanatory notes.

Cracking

In all runs severe cracking of the cylinders occurred during the reaction. On occasion small pieces of the product flaked away from the main agglomerate.

Percentage Conversion

The results quoted in Table 2 for the percentage conversions were calculated from the sample weights before and after the reaction, when one assumes that the gaseous reaction product is solely carbon monoxide. In several of the runs conversions slightly greater than 100% were thus calculated. These high values were probably caused by loss of weight arising from slight spalling of the sample during reaction. In runs 2, 3, 4, 7, and 8 no carbon dioxide was evolved on treating the slaked product with hydrochloric acid. The amount of carbonate present was therefore negligible, and complete conversion was confirmed. In the other runs carbonate was present in the final product according to the hydrochloric acid test.

Reaction Time

The reaction time was taken as the total time during which gas evolution occurred, as indicated by a capillary flow meter. Even though the rate of gas evolution was low at the final stages of reaction, it was possible to determine the cessation of flow to within ±0.1 hr. In runs 5 and 6, in which incomplete decomposition was obtained, the reaction rate had decreased to a very low value at the time the run was terminated.

The product obtained from the runs in which graphite was used was harder and less porous than that obtained from the studies with carbon black.

DISCUSSION

When a carbon black was admixed with the barium carbonate, time-temperature curves similar to those in Figure 1 were obtained. The internal temperature, which is equal to the reaction temperature (see reference *6*), remained practically constant for almost the entire reaction.

However when a natural graphite such as Dixon Microfyne was mixed with the barium carbonate, time-temperature curves similar to Figure 2 were obtained. The center temperature rose continuously, and the temperature difference available for heat transfer from the furnace to the reaction zone decreased steadily with time. Relatively low rates of reaction were obtained, and the internal reaction temperatures measured were higher than those observed with the runs with carbon black. The reduced rate of decomposition resulting from the use of graphite was presumably caused by either one or a combination of the following factors: (1) larger particle size of the natural graphite, and (2) the difference between the reactivity of the more crystalline graphite vs. that of the more amorphous carbon black.

To determine the relative importance of each of these factors rate determinations were made with each of two samples of carbon black which had similar particle sizes but different physical structures. The first run of this pair (run 7) used a sample of Sterling FT which previously had been heated in a nitrogen atmosphere for 2 hr. at 2,700°C. The resulting black was found to have

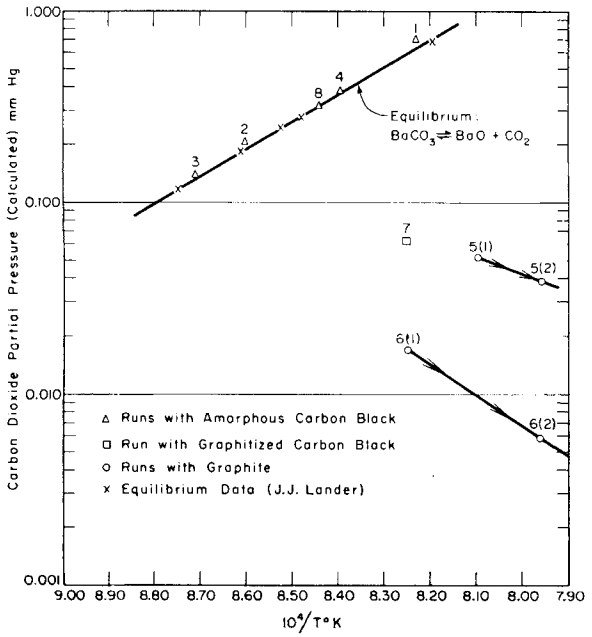

Fig. 3. Comparison of CO_2 partial pressures calculated from experimental data with those for equilibrium conditions.

a B.E.T. surface area of 12.7 sq. m./g. and gave an X-ray diffraction pattern which indicated that substantial graphitization had taken place. The second run (run 8) contained untreated Sterling FT carbon black which had a B.E.T. surface area of 15.7 sq. m./g. The results of the two runs are compared in Table 2.

The data show that, even though a higher pressure was maintained in run 8, the reaction temperature was lower and the time for complete reaction was much less than in run 7. It is apparent that use of a more amorphous carbon considerably accelerates the over-all reaction rate over that obtainable with graphitized carbon.

It is reasonable to assume that reaction 2 is the result of reactions 1 and 3 in series.

$$BaCO_3 \rightarrow BaO + CO_2 \qquad (3)$$

Consequently for finite reaction rates the measured pressure and reaction temperature may approximate those of equilibrium for both reactions 1 and 3, for either one of the reactions, or for neither. To compare the experimental conditions with equilibrium values the partial pressure of carbon dioxide that would be present if reaction 1 were occurring at equilibrium was calculated from the equilibrium constant for reaction 1 (*4*) and the experimental value for the total pressure. (Solid carbon is present at all times, and only carbon dioxide and carbon monoxide are present in the gas phase, carbon monoxide being overwhelmingly predominant.)

If reactions 1 and 3 both took place at equilibrium, the value of the carbon dioxide partial pressure thus calculated would equal that reported for equilibrium for reaction 3. If one or both of the reactions occurred under nonequilibrium conditions, the calculated pressure would be less than the equilibrium value. The comparison is made in Figure 3. It is seen that all the runs with carbon black occurred under equilibrium conditions; indeed the agreement with Lander's data is remarkably good. This means that the rate at which decomposition occurred was controlled completely by the rate of heat transfer to the reaction zone and was unaffected by mass transfer or chemical reaction kinetics. The time-temperature curves for all these runs were of the type shown in Figure 1, which is the same type as that obtained in an earlier study of the decomposition of cylinders of compacted calcium carbonate agglomerates of small particle size, a process which previously has been shown to occur under conditions approximating those of equilibrium (*6*).

For the runs with natural graphite the reaction temperature rose steadily, and the calculated carbon dioxide partial pressures are given in Figure 3 for two temperatures, when decomposition commenced and after 1 hr. (These are indicated by points 1 and 2 on Figures 2 and 3.) With partially graphitized carbon black a substantial fraction of the reaction occurred at a temperature of about 1,720° to 1,730°F., indicated by a square on Figure 3. It is evident that with graphite the rate of reaction 1 becomes much slower than with carbon black, and a comparison of runs 7 and 8 shows that this is not caused by gross particle size or total surface area of the particles but must rather reflect a much greater reactivity of carbon black surfaces over that of graphite.

Smith and Polley (*7*) recently have studied the rate of oxidation in air of Sterling FT carbon black before and after graphitization. After graphitizing at 2,700°C. they found it necessary to increase the reaction temperature to 800° to 900°C. to achieve the same rate of oxidation as that obtained with the original carbon black at 600°C. This change in chemical reactivity was related to the nature of the surface as revealed by physical adsorption and other methods; for example the carbon black particles were found to develop considerable porosity as indicated by a substantially increased area after reaction, while there was little change in area of the graphiticized carbon. On the other hand this moderate increase in area is insufficient to explain the enormous difference between the reactivities of the two carbons. Smith and Polley concluded that oxygen attack occurred preferentially at specific high-energy sites on the surface that may be edge-carbon atoms in the layer lattice, the number of these sites being greatly reduced by the heat treatment. The reactivity of the various forms of carbon to carbon dioxide in the present work exactly parallels the results they reported on comparative reactivity to oxygen and can be interpreted in the same way.

The extent to which this or any other decomposition reaction is controlled by heat transfer vs. some kinetic process is, of course, determined by many factors, the most important of which are the size of the mass being studied, the rate of heat transfer to the mass, the sizes of the individual particles, their compactness, and their reactivities. These studies show, for a few combinations, the relative importance of some of these variables in their effect on the over-all observed rate of reaction.

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