Carbon-catalysed Exchange Between Carbon Dioxide and Potassium Carbonate at 500—1000 K

John M. Saber,[a] John L. Falconer,*[a] and Lee F. Brown[b]

[a] *Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309, U.S.A.*

[b] *Earth and Space Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.*

Between 500 and 1000 K, well below where the carbonate-catalysed C–CO_2 reaction occurs, potassium carbonate–carbon mixtures in carbon dioxide gas exchange carbon and oxygen between the CO_2 and K_2CO_3, with two labile surface carbonate complexes as probable intermediates.

Because of the importance of the carbonate-catalysed carbon-oxidation reactions, much attention has been given to interactions among carbon, alkali-metal, or alkaline-earth carbonates, and various oxidants at temperatures where oxidation of the carbon occurs.[1] This communication reports interactions which occur in the K_2CO_3–C–CO_2 system at temperatures well *below* the onset of carbon oxidation. The interaction of a Cabot oil-based carbon black and isotopically-labelled potassium carbonate was studied in flowing CO_2 (*ca.* 0.1 atm.) between 500 and 1000 K. Physical mixtures of carbon (100 mg) and potassium carbonate (10 mg) were outgassed at 500 K and 4 Pa for 30 minutes, then subjected to

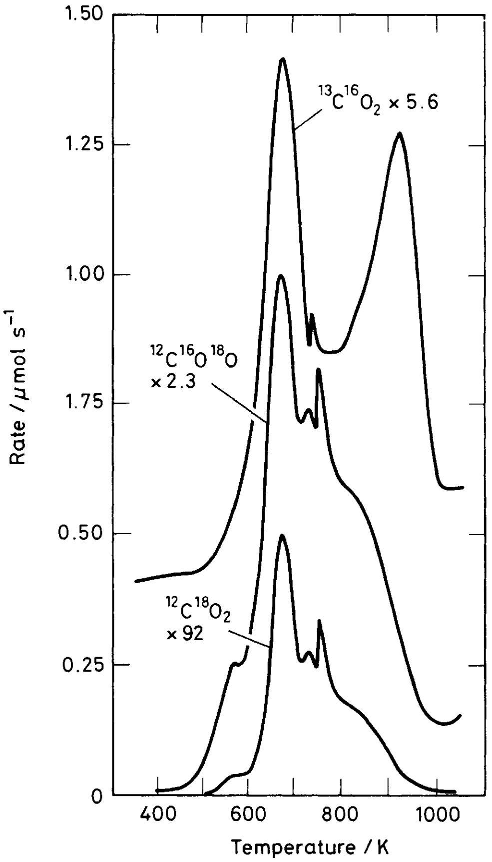

Figure 1. Changes in $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$, and $^{12}C^{18}O_2$ mass signals during TPR of $K_2{}^{13}C^{16}O_3$–^{12}C (10:100 mg) and $K_2{}^{12}C^{18}O_3$–^{12}C (10:100 mg) mixtures in $^{12}C^{16}O_2$–He flow. (For clarity, the $^{13}C^{16}O_2$ trace is displaced upward by 0.4 µmol s^{-1}).

temperature-programmed reaction (TPR) by heating the mixture at 1 K s^{-1} in flowing 10% CO_2–90% He. The gaseous products were detected with a mass spectrometer which could measure up to five mass peaks simultaneously. Some experiments used K_2CO_3 containing ^{13}C (of the C in the K_2CO_3, 90 atom % was ^{13}C); in others the carbonate contained ^{18}O (of the O in the K_2CO_3, 70.5 atom % was ^{18}O); a third series used normal potassium carbonate ($K_2{}^{12}C^{16}O_3$) and carbon black containing ^{13}C. An additional experiment substituted silica for the carbon black; others used pure carbonate, carbon, or equal amounts of carbon–carbonate. In all experiments, the flowing gas contained no tracers.

Figure 1 shows typical results from tests involving the 10 mg of labelled carbonates and 100 mg C. Shown are traces of the $^{13}CO_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ in the effluent gas between 500 and 1000 K. The $^{13}CO_2$ curve was obtained in a test using $K_2{}^{13}CO_3$. The traces correspond to the rate at which labelled carbon dioxide appeared in the gas phase, and the areas under the curves are proportional to the amount of carbon dioxide formed. For each experiment, the $^{12}C^{16}O_2$ traces were mirror images of those in Figure 1, and material balances indicated that no net change occurred in the atomic composition of the solid mixtures. The figure thus shows that carbon and oxygen in the gas-phase carbon dioxide exchanged with carbon and oxygen in the carbonate, and that there was no net decomposition of the carbonate.

A mixture of K_2CO_3–SiO_2 (10:100 mg) showed no exchange when heated in CO_2. Hence carbon is needed to induce the exchange reactions. On the other hand, in the experiments with the ^{13}C in the solid carbon, no ^{13}C appeared in the gas-phase CO_2. This means that the carbon acted as a true catalyst in promoting the exchanges; its presence was necessary for the exchanges to occur, but the carbon itself did not exchange. It follows from these observations that some complex or complexes were formed involving the carbon substrate which acted as intermediates in the exchange process. When a $K_2C^{18}O_3$–$K_2C^{16}O_3$–C (25:100:125 mg) mixture was heated in flowing 10% CO_2–90% He, not only did exchange occur but a significant net amount of CO_2 was adsorbed from the gas phase, in contrast to the situation when only a small amount of carbonate was present. When pure carbonate was heated in flowing 10% CO_2–90% He, however, CO_2 did not adsorb to a detectable extent, nor did any exchange occur. Similarly, when pure carbon was heated in CO_2–He, CO_2 absorption was not detected.

The $^{13}CO_2$ curve in Figure 1 is quite different from the curves for $C^{16}O^{18}O$ and $C^{18}O_2$. The exchange of carbon atoms (measured by $^{13}CO_2$ formation) occurred in two distinct temperature ranges, one centred at 675 K and the other at 925 K. The $^{13}CO_2$ peaks at two different temperatures indicate two activation energies, which imply the existence of two different complexes as intermediates for the exchanges. Oxygen atom exchange (measured by $C^{16}O^{18}O$) peaked at 675 K, then declined, with intermittent peaks, throughout the remaining temperature span. Thus rates for carbon and oxygen exchange were not the same. The ratio of the total amount of carbon to oxygen exchanged was equal to the ratio of the amount of ^{13}C and ^{18}O in the carbonates, and about 90% of the labelled atoms came off in the gas. These observations mean that essentially all of the carbonate was available for exchange and that both the carbon and the oxygen were exchanged to the same extent. The ratio of $C^{16}O^{18}O$ to $C^{18}O_2$ in the effluent gas was 80:1. The presence of these large amounts of $C^{16}O^{18}O$ relative to $C^{18}O_2$ in the effluent gas means that most of the carbon–oxygen bonds in the carbonate broke and reformed during the exchange. That is, oxygen was readily exchanged between the carbon dioxide molecules and the carbonate. The differences in the $^{13}CO_2$ and $C^{16}O^{18}O$ traces were additional indications of this behaviour.

The carbon surface could not be subjected to rigorous cleaning procedures before these experiments because of the presence of the carbonate. Thus it almost unquestionably was covered with a surface oxide coating.[2] When $K_2C^{18}O_3$ (10 mg) and carbon black (100 mg) were heated in helium alone to 1250 K, the total amount of oxygen that appeared in the exit gases was greater than was in the K_2CO_3, supporting the assumption of oxygen on the carbon surface. The $C^{16}O^{18}O$–$C^{18}O_2$ ratio in this last experiment also indicated that surface oxides exchanged oxygen with the oxygen in the carbonate, although not to the extent observed in the oxygen exchanges between the gaseous CO_2 and carbonate when CO_2 was in the flowing gas.

It thus appears that metastable states form, and these states involve both the potassium carbonate and the oxide already on the carbon surface. *Via* these states, the potassium carbonate is converted to a form, such as an oxide, that is able to adsorb CO_2 from the gas phase. As noted above, if the oxide-covered carbon surface is not present, the potassium compound is not able to take the CO_2 from the gas phase. Dentates may well be involved here. Many studies show that carbonate complexes form on oxide surfaces,[3–6] that the monodentate and bidentate forms are most common,[3,4] and that the two forms frequently coexist.[6] Oxide surfaces were present, with both the potassium and the carbon. Surface monodentate and bidentate forms decompose at different temperatures,[6] which would account for the two peaks observed. The extensive oxygen exchange when gaseous CO_2 is present would occur because of the weak oxygen bonding that has been observed in both monodentate and bidentate complexes.[6]

All these effects were observed well below onset of the C–CO_2 reaction, which began at about 1050 K for K_2CO_3–C (10 : 100 mg) in 10% CO_2–90% He. Thus, physical mixtures of carbonate combined with carbon can interact with gaseous CO_2 at temperatures as low as 500 K; exchange of both oxygen and carbon atoms between the carbon dioxide and the carbonate can occur, and at different rates. It is postulated that this happens because metastable states are formed involving the potassium carbonate, the oxygen on the carbon surface, and carbon dioxide from the gas phase. The carbon and oxygen exchange *via* dentate complexes. The dentate complexes promote rapid oxygen exchange and decompose at different temperatures, accounting for the principal features of the exchanges.

We gratefully acknowledge support of this work by the Department of Energy. We also thank Kevin G. Wilson for his assistance.

Received, 7th December 1983; Com. 1593

References

1 D. W. McKee and J. T. Yates, Jr., *J. Catal.*, 1981, **71**, 308; T. Wigmans, R. Elfring, and J. A. Moulijn, *Carbon,* 1983, **21**, 1.
2 H. P. Boehm, *Adv. Catal.*, 1966, **16**, 181.
3 M. L. Hair, 'Infrared Spectroscopy in Surface Chemistry,' Dekker, New York, 1967, pp. 204—208.
4 H. Knözinger, *Adv. Catal.*, 1976, **25**, 234.
5 C. Morterra, S. Coluccia, G. Ghiotti, and A. Zecchina, *Z. Phys. Chem. (N.F.),* 1977, **104**, 275.
6 G. Busca and V. Lorenzelli, *Mat. Chem.*, 1980, **5**, 213; 1982, **7**, 89.