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A SIMS Study of the Interaction of Potassium Carbonate with Carbon Black

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Secondary ion mass spectrometry combined with isotopic labeling has been applied to study the interaction of potassium carbonate ($K_2C^{18}O_3$) with carbon black (^{13}C) at 300–1500 K. The SIMS analysis shows that K_2CO_3 decomposes above 800 K to form K_2O, which subsequently decomposes at 1070 K. A K_2O surface species was identified by SIMS at all the temperatures studied. The presence of K_2O before K_2CO_3 thermally decomposes is attributed to the presence of H_2O in the original sample, and a model is presented to explain K_2O formation. © 1990 Academic Press, Inc.

INTRODUCTION

Potassium carbonate, one of the most effective catalysts for coal gasification, interacts with carbon to form an active catalytic complex (*1*). As shown by their ability to exchange CO_2, such complexes form below gasification temperatures (*2, 3*). Both Freriks *et al.* (*4*) and Mims and Pabst (*5, 6*) proposed that a K–O–C structure forms when K_2CO_3 reacts with carbon. Mims and Pabst (*5*) concluded that the surface K–O–C groups were at aromatic edge sites, and others (*7–9*) have proposed similar complexes. Metallic potassium has also been suggested as an intermediate, however. Potassium metal was observed at gasification temperatures directly by Knudsen cell mass spectrometry (*8*), and potassium metal was observed on reactor walls following gasification (*2, 10*).

In contrast, Yokoyama *et al.* (*11*), using XPS measurements of K_2CO_3/C samples, observed that K_2CO_3 decomposes at 925 K to form K_2O. The K_2O was reduced by carbon at higher temperatures to form metallic potassium. Saber *et al.* (*12*) also proposed, on the basis of stoichiometry measurements in TPD/TPR experiments, that a K_2O intermediate formed. They argued, however, that during an oxidation/reduction mechanism, the potassium cycled between K_2O and K_2O_2.

We carried out secondary ion mass spectrometry experiments (SIMS) to obtain a direct measurement of the surface species present in K_2CO_3/C mixtures. These mixtures were heated in UHV and their surface compositions measured as a function of temperature. The oxygen in the carbonate and the carbon in the substrate were isotopically labeled in order to trace the reaction pathways. We find that K_2CO_3 decomposes in the presence of carbon above 800 K to form K_2O, and that the K_2O subsequently decomposes under vacuum above 1070 K. We also show that water on the carbon black apparently causes some K_2CO_3 to dissociate to form K_2O when the K_2CO_3/C sample is prepared at room temperature. A mechanism for the room temperature dissociation of K_2CO_3 on carbon black in the presence of water is discussed.

EXPERIMENTAL

The sample used in this study consisted of 2.5 mol% $K_2C^{18}O_3$ and 97.5 mol% ^{13}C-labeled carbon black. The $K_2C^{18}O_3$ (Prochem, Inc.) had a minimum isotope purity of 71.5 at.% ^{18}O, and the carbon black (Isotec, Inc.) was 99% ^{13}C enriched. The $K_2C^{18}O_3$/^{13}C sample was prepared by physi-

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cally mixing the $K_2C^{18}O_3$ and ^{13}C components and then mechanically pressing the mixture into a 1-cm-diameter pellet with a force of 8000 N. Both the $K_2C^{18}O_3$ and the ^{13}C were used as received. The sample contained some water since a small amount of liquid water was observed around the sample after it was pressed into a pellet.

The SIMS experiments were performed in a two-level turbomolecular-pumped, stainless-steel UHV chamber (base pressure = 5×10^{-10} Torr). The sample was bombarded at normal incidence by a 4.5-keV primary Ar^+ ion beam, which had a current density of 1×10^{-7} A/cm^2. The Ar^+ ion beam was generated by a Colutron Model G-2 ion gun and was mass analyzed by a Wien-type velocity filter. The ion beam was collimated to a diameter of 2.4 mm by a grounded aperture located in front of the sample. The secondary ions emitted from the surface were accepted into a Bessel box energy analyzer and were subsequently mass analyzed by an Extranuclear Laboratories quadrupole mass spectrometer. Both positive and negative secondary ions were detected using pulse counting techniques. The pass energies were 8.0 eV for positive ions and 3.3 eV for negative ions. The energy band width was about ±2.0 eV for both positive and negative ions.

The sample was mounted on a sample manipulator located in the UHV system and the sample temperature was monitored by a Chromel–Alumel thermocouple located adjacent to the sample on the sample holder. The sample was heated by electron bombardment and radiation from a W filament located behind the sample. Sample temperatures up to 1600 K could be achieved.

RESULTS AND DISCUSSION

SIMS Spectra of $K_2C^{18}O_3/^{13}C$ at Room Temperature

To establish the chemical composition of the surface prior to thermal treatment, we examined the SIMS spectra of the $K_2C^{18}O_3/^{13}C$ sample, as prepared, at room temperature. The positive and negative ions SIMS spectra are shown in Fig. 1. Table 1 presents selected ratios of secondary ion intensities from Fig. 1 after correction for mass spectrometer sensitivity, which is inversely proportional to the square of the mass. The ^{13}C hydrocarbon ions seen in both spectra indicate the presence of ^{13}C hydrocarbon species intrinsic to the ^{13}C carbon black. Since the carbon black is specified to contain only 1% ^{12}C, the ^{12}C and $^{12}C^-$ hydrocarbon ions that appear in both spectra suggest that some hydrocarbon species have adsorbed onto the sample from the atmosphere.

The presence of water on the sample surface is reflected directly by the appearance of the $H_2^{16}O^+$ and $H_2^{18}O^+$ ions (Fig. 1). The $H_2^{18}O^+$ ion shows that some surface water is derived from oxygen that was originally associated with $K_2C^{18}O_3$. However, since the observed $H_2^{18}O^+/H_2^{16}O^+$ ratio of 1.1 is well below 2.4, which corresponds to the $^{18}O/^{16}O$ ratio of the carbonate (based on the specified isotope purity of 71.5 atm% ^{18}O in the K_2CO_3), much of the surface water is derived from noncarbonate oxygen. The presence of surface water derived from

TABLE 1

Ion Intensity Ratios at Room Temperature

Ion ratio	Intensity ratio
$K_2^{18}O^+/K_2^{16}O^+$	2.4
$K^{18}O^+/K^{16}O^+$	1.0
$K^{18}O^-/K^{16}O^-$	1.3
$K_2^{18}O^+/K^{18}O^+$	140
$K_2^{16}O^+/K^{16}O^+$	120
$^{18}O^-/^{16}O^-$	1.2
$^{18}OH^-/^{16}OH^-$	0.95
$H_2^{18}O^+/H_2^{16}O^+$	1.1
$H_2^{18}O^+/^{18}OH^-$	0.45
$H_2^{16}O^+/^{16}OH^-$	0.44

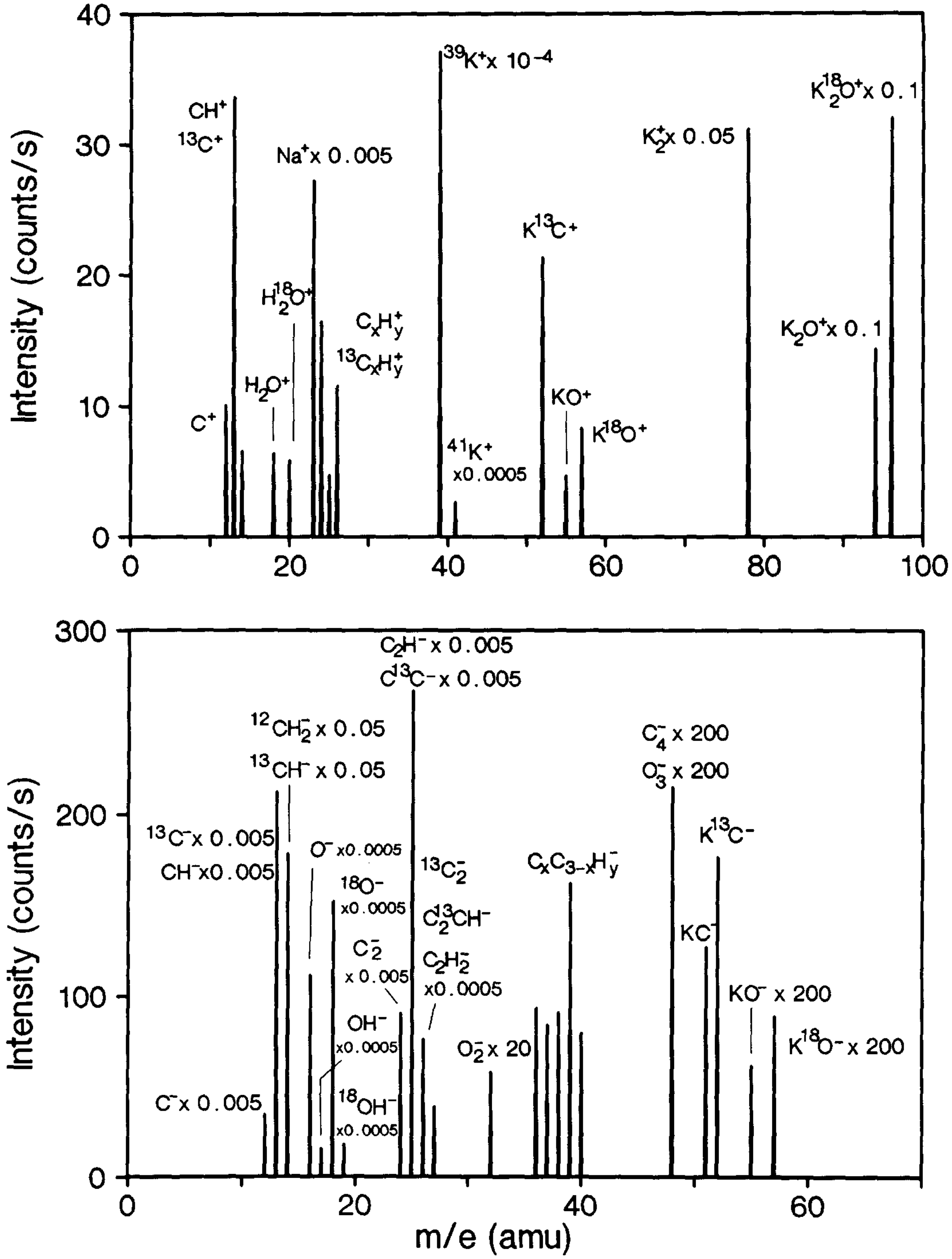


FIG. 1. Positive and negative SIMS spectra of the $K_2C^{18}O_3/^{13}C$ mixture at 300 K. Standard deviations of the $K^{18}O^+$, $K_2^{18}O^+$, $H_2^{18}O^+$, $^{18}O^-$, $^{18}OH^-$, and $K^{18}O^-$ signals are 15, 5, 15, 5, 5, and 15%, respectively.

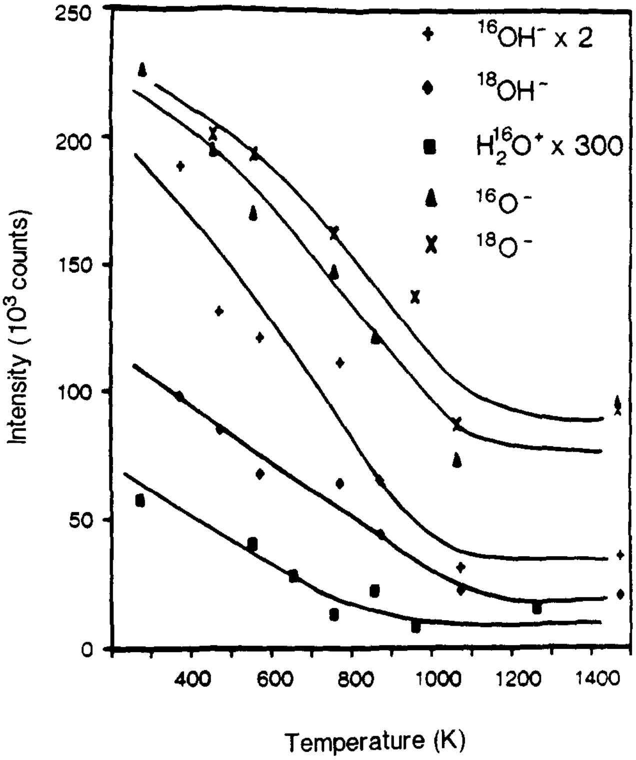


FIG. 2. Temperature dependences of the $H_2^{16}O^+$, $^{16}OH^-$, $^{18}OH^-$, $^{16}O^-$, and $^{18}O^-$ secondary ion signals for the $K_2C^{18}O_3/^{13}C$ mixture. Standard deviations of the $H_2^{16}O^+$, $^{16}OH^-$, $^{18}OH^-$, $^{16}O^-$, and $^{18}O^-$ signals are 15, 5, 5, 5, and 5%, respectively.

noncarbonate oxygen is consistent with the water observed when the sample was prepared. Much of this water presumably originated by adsorption of water from the atmosphere onto the sample components. The water that contains carbonate oxygen probably forms by an oxygen exchange reaction between the carbonate and the surface water that originated from the atmosphere. This suggestion is supported by results described below.

The $^{16}O^-$ and $^{18}O^-$ ions reflect the presence of surface oxygen species, but not their specific chemical states or environments. We note, however, that the $^{18}O^-/^{16}O^-$ intensity ratio is nearly identical to that of the $H_2^{18}O^+/H_2^{16}O^+$ ratio (see Table 1). This suggests that most of the surface oxygen contributing to the O^- signal is derived by fragmentation of surface water molecules. This interpretation is supported by results presented in Fig. 2, which show the intensity variations of the $H_2^{16}O^+$, $^{16}O^-$, $^{18}O^-$, $^{16}OH^-$, and $^{18}OH^-$ ions as a function of increasing sample temperature. In this experiment, the ion intensities were measured after sequentially heating the sample to successively higher temperatures and maintaining the sample at that temperature for 5 min. The rapid decrease of the $H_2^{16}O^+$, and $H_2^{18}O^+$ ion intensities between 300 and 1000 K correlates with the desorption of water observed in previous TPD measurements on a sample prepared with the same carbon black. The O^- ions decrease essentially in proportion with the H_2O^+ ions during the desorption of water, while the $H_2^{18}O^+/H_2^{16}O^+$, $^{18}OH^-/^{16}OH^-$, and $^{18}O^-/^{16}O^-$ isotope ratios remain nearly constant and equal to 1.1. The strong correlation of the intensity variation and the virtually identical isotopic distribution of the O^- and H_2O^+ ions during the thermal desorption of water imply that most of the surface oxygen that contributes to the O^- ion signal is derived by fragmentation of surface water molecules.

Similarly, the $^{16}OH^-$ and $^{18}OH^-$ ions appear to be derived primarily from fragmentation of water and not from hydroxyl groups. The $^{16}OH^-$ and $^{18}OH^-$ ion intensities decrease in proportion with the H_2O^+ ions during heating, and the $^{18}OH^-/^{16}OH^-$ ratio remains nearly equal to the $H_2^{18}O^+/H_2^{16}O^+$ ratio.

Although the sample contains $K_2C^{18}O_3$, most of the oxygen contributing to the O^- signal comes from surface water, not from the carbonate. Since compensation for sample charging was not used in the SIMS experiments, differential charging of the nonconducting $K_2C^{18}O_3$ component probably prevents the detection of ions emitted from the carbonate and thereby prevents any contribution from the carbonate to the O^- signal. Indeed, no CO_3^- ions are observed in the SIMS spectrum of the $K_2C^{18}O_3/^{13}C$ sample, and when charge compensation was not used, no secondary ions of any type were observed during SIMS measurements of a pure $K_2C^{18}O_3$ sample. Likewise, no ^{13}C ions were observed in a SIMS study of a physical mixture of $Ca^{13}CO_3$ with ^{12}C carbon black (*13*). Most of the ions detected in the SIMS measurements, therefore, are apparently emitted only from the surface of the carbon black, since it is a relatively good conductor and hence less susceptible to charging than carbonates.

The parallel decrease of the ^{16}O- and ^{18}O-labeled ions in Fig. 2 suggests that $H_2^{16}O$ and $H_2^{18}O$ have nearly the same distribution of binding energies to the surface and therefore probably exist in similar chemical environments. The virtually identical values of the $H_2^{16}O^+/^{16}OH^-$ and $H_2^{18}O^+/^{18}OH^-$ ratios (Table 1) further confirm this conclusion since molecular dynamics simulations of the ejection processes (*14*) and experimental measurements (*15*) indicate that the yield ratios of ejected parent molecules to ejected fragments thereof are sensitive to the intra- and intermolecular bond strengths and to the binding site geometry of the parent molecule. If the $H_2^{16}O$ and $H_2^{18}O$ molecules were in different electronic environments, one would also expect different values of the $H_2^{16}O^+/^{16}OH^-$ and $H_2^{18}O^+/^{18}OH^-$ ratios because the ionization probabilities for positive and negative ion formation tend to vary in opposite directions with variations in the local electronic structure of the surface. The similarity of the surface chemical states of $H_2^{16}O$ and $H_2^{18}O$ further supports the suggestion that $H_2^{18}O$ forms by an oxygen exchange between the carbonate and the $H_2^{16}O$ that adsorbed from the atmosphere.

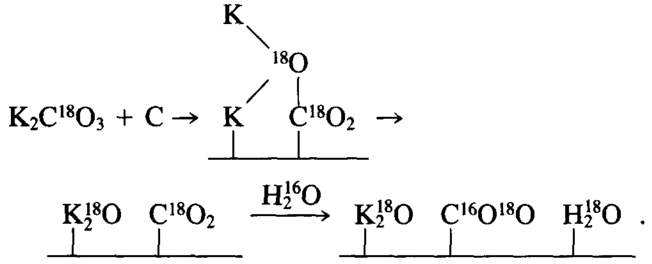
Also of interest in the SIMS spectrum is the appearance of the $K_2^{18}O^+$, $K_2^{16}O^+$, $K^{18}O^+$, $K^{16}O^+$, $K^{18}O^-$, and $K^{16}O^-$ ions. Several types of surface species could conceivably be responsible for emission of these ions, since they can, in principle, form by several mechanisms. For example, molecular dynamics simulations of the ejection process in SIMS (*15, 16*) and recent SIMS measurements (*17, 18*) indicate that bound molecular surface species and fragments thereof can often be emitted from the surface intact. The observed K_2O^+ and KO^+ ions could thus be derived by intact emission and simple fragmentation, respectively, of surface K_2O molecules. Another possibility is that the K_2O^+ and KO^+ ions might be formed by a mechanism involving recombination of K and O atoms that are emitted independently. Both theory (*15, 19, 20*) and experiment (*15, 16, 21, 22*) suggest that this mechanism will dominate the formation of K_2O^+ and KO^+ if K and O atoms are located in close proximity to each other on the surface (typically 0.1–1.0 nm) without being associated as bound molecular K_2O and KO entities. A combination of intact emission and recombination processes may also be involved. For example, if molecular KO but not K_2O surface species were present, the KO^+ ions could be derived by intact emission of surface KO molecules while K_2O^+ could form by recombination of intact KO molecules/ions and K atoms/ions.

The K-containing ion ratios in Table 1 contain additional information which strongly indicates that the K_2O^+ ions are derived primarily by intact emission of molecular K_2O surface species while the KO^+ ions are derived by both fragmentation of the K_2O surface species and in part by recombination of independently emitted K and O atoms. Specifically, we first note that the $K_2^{18}O^+/K_2^{16}O^+$ ratio of 2.4 is the same as the $^{18}O/^{16}O$ ratio of the starting potassium carbonate. This shows that the $K_2^{18}O^+$ and $K_2^{16}O^+$ ions are derived exclusively from oxygen atoms originally associated with the carbonate and not from a recombination process involving oxygen atoms from another source. The $K_2^{18}O^+$ and $K_2^{16}O^+$ ions must therefore form either by intact emission of surface K_2O species that are derived exclusively from carbonate oxygen or by a recombination process that involves carbonate oxygen only. The $K^{18}O^+/K^{16}O^+$ and $K^{18}O^-/K^{16}O^-$ ratios are substantially less than 2.4 and thus the KO^+ and KO^- ions form from both noncarbonate and carbonate oxygen. Since the major source of the noncarbonate oxygen is water, most of the KO^+ and KO^- ions that contain noncarbonate oxygen probably form by recombination of independently emitted K and O atoms, in which the O atoms are derived by fragmentation of water. Since noncarbonate oxygen can apparently be incorporated into KO^+ and KO^- ions through a recombination process, one would expect that noncarbonate oxygen would also be incorporated into some K_2O^+ ions if they were formed by a recombination process. The absence of any detectable K_2O^+ ions derived from recombination processes involving noncarbonate oxygen atoms therefore indicates that K_2O^+ ions are not derived by a recombination process, but rather by intact emission of K_2O surface species that are derived exclusively from carbonate oxygen.

Both theory (*23*, *24*) and experiment (*24*) indicate that the probability of forming molecular ions by recombination of independently emitted particles often tends to decrease as the number of particles that recombine increases. Indeed, some KO^+ ions but no detectable K_2O^+ ions appear to form by recombination mechanisms. If the K_2O^+ ions that appear in the SIMS spectra were formed by recombination, one would expect the K_2O^+/KO^+ ratio to be less than 1. The large values of the $K_2^{18}O^+/K^{18}O^+$ and $K_2^{16}O^+/K^{16}O^+$ intensity ratios (Table 1) thus support the concept that the $K_2^{18}O^+$ and $K_2^{16}O^+$ ions are most likely formed by intact emission of surface K_2O species.

We finally note that while the $K^{18}O^+/K^{16}O^+$ and $K^{18}O^-/K^{16}O^-$ ratios are less than 2.4, which corresponds to the $^{18}O/^{16}O$ ratio of the carbonate, they are greater than 1.1, which corresponds to the $H_2^{18}O^+/H_2^{16}O^+$ ratio. This indicates that some KO^+ and KO^- ions are derived from recombination processes involving oxygen derived from surface water while other KO^+ and KO^- ions are derived by simple fragmentation of surface K_2O species.

As shown below, K_2O forms by thermal decomposition of K_2CO_3 only above 800 K; the K_2O observed by SIMS at 300 K must therefore be derived by another mechanism. The presence of $H_2^{18}O$ suggests that K_2O at 300 K results from an interaction between surface water ($H_2^{16}O$) and $K_2C^{18}O_3$. The formation of K_2O, which is derived exclusively from carbonate oxygen, can be explained by the following process:



In this model, hydration or solvation of some of the $K_2C^{18}O_3$ by surface water allows some potassium and carbonate ions to migrate onto the carbon surface where they interact with each other to form K_2O and adsorbed CO_2. The oxygen in the K_2O formed by this mechanism thus originates exclusively from the carbonate, as observed. The $H_2^{18}O$ forms by exchange of oxygen between $H_2^{16}O$ and the $C_2^{18}O_2$ that forms from the carbonate. We note that $H_2^{16}O$ cannot exchange oxygen directly with the $K_2C^{18}O_3$, since subsequent decomposition of the carbonate would then lead to the formation of some K_2O in which the oxygen originated from $H_2^{16}O$. This is inconsistent with the observation that K_2O is derived exclusively from carbonate oxygen. The exchange of oxygen between CO_2 and water is consistent with the observations of Saber *et al.* (*2, 3*), who showed that the CO_2 from the gas phase can adsorb onto $K_2C^{18}O_3$/carbon black samples and exchange oxygen with surface species.

The formation of CO_2 at 300 K, by the interaction of the carbonate with adsorbed water, is also consistent with the previous TPD measurements of Saber *et al.* (*25*) shown in Fig. 3a. The upper TPD curve (curve A) shows that when K_2CO_3 is physically mixed with the same water-containing carbon black used in this study, a $^{13}CO_2$ thermal desorption peak occurs at about 450 K. In agreement with results presented above, this suggests that some carbonate decomposes to form $^{13}CO_2$ below the onset of thermal decomposition of the carbonate. The $^{13}CO_2$ peak at 500 K is believed to correspond to the decomposition of some potassium bicarbonate that is present in the K_2CO_3 starting material and is known to thermally decompose in this temperature region (*26*). Saber *et al.* (*25*) showed that most of the $^{13}CO_2$ that desorbs between 550 and 1000 K results from isotope exchange between $K_2^{13}CO_3$ and $^{12}CO_2$ from the carbon black, but desorption of $^{13}CO_2$ above 1000 K results from thermal decomposition of the carbonate. In contrast, curve B of Fig. 3a shows that the $^{13}CO_2$ peak at 450 K is absent for samples prepared by physically mixing $K_2^{13}CO_3$ with pyrolyzed carbon black, which contains little or no water. These results thus suggest that the formation of CO_2 derived from the carbonate, at temperatures below the thermal decomposition temperatures of the carbonate, occurs only when water is present, which is in accord with the mechanism proposed above.

Thermal Treatment

The surface chemistry of the $K_2C^{18}O_3/^{13}C$ mixture was monitored by observing the intensity variations of several SIMS ions as a function of increasing sample temperature. The ion intensities were monitored after subsequentially holding the sample at successively higher temperatures for 5 min (Fig. 3b). The $K_2^{18}O^+$ and $K_2^{16}O^+$ intensities were essentially constant until 800 K, at which point they increased rapidly to a maximum near 1100 K. The intensities then decreased as the temperature increased

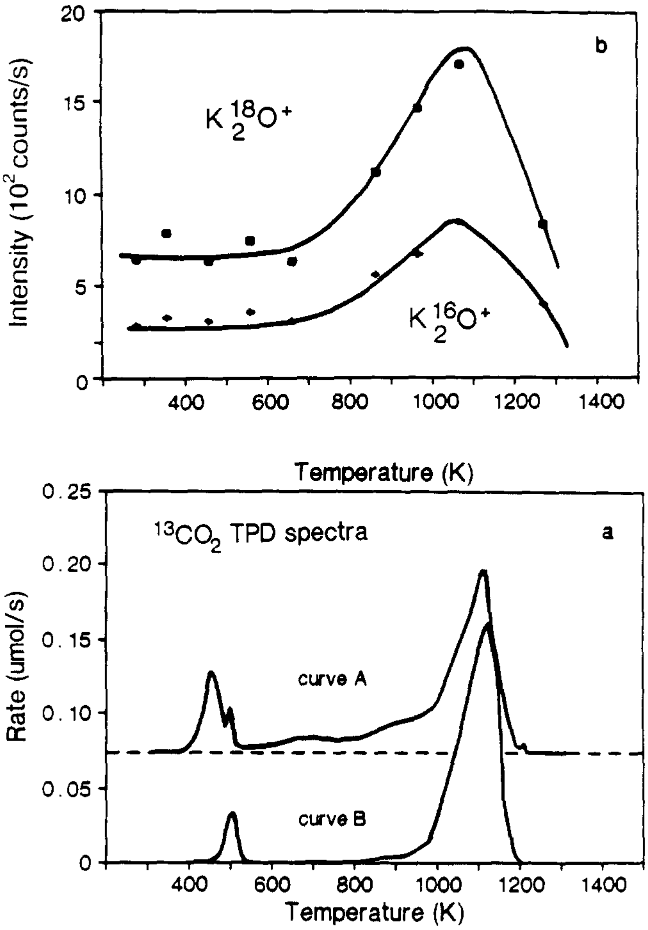


FIG. 3. (a) $^{13}CO_2$ TPD spectra for mixtures of: (A) 10 mg $K_2^{13}CO_3$ and 100 mg Sterling RX-76 carbon (0.6% volatiles) and, (B) 10 mg $K_2^{13}CO_3$ and 100 mg pyrolyzed Regal carbon (*12*). (b) Temperature dependence of the $K_2^{18}O^+$ and $K_2^{16}O^+$ secondary ion signals for the $K_2C^{18}O_3/^{13}C$ mixture. Standard deviations of the $K_2^{18}O^+$ and $K_2^{16}O^+$ signals are 5 and 5%, respectively.

from 1100 to 1300 K. Up to 1300 K the $K_2^{18}O^+/K_2^{16}O^+$ ratio was essentially constant at about 2.4, which corresponds to the $^{18}O/^{16}O$ ratio of the carbonate.

The growth of the K_2O^+ intensities above 800 K correlates with the high-temperature $^{13}CO_2$ peaks of the TPD spectra in Fig. 3a. Since these TPD peaks result from $^{13}CO_2$ decomposition (*25*), the SIMS result indicates that K_2O is a surface product of K_2CO_3 decomposition. The essentially identical values of the $K_2^{18}O^+/K_2^{16}O^+$ ratio and the $^{18}O/^{16}O$ ratio of the original carbonate indicate that the surface K_2O species are derived exclusively from carbonate oxygen. The surface K_2O species apparently do not undergo oxygen exchange with noncarbonate oxygen sources up to 1300 K.

The decrease in the K_2O^+ intensity above 1100 K is apparently due to thermal decomposition of the surface K_2O species to form potassium metal. Several workers (*2, 10, 27*) have observed potassium metal on reactor walls following K_2CO_3-catalyzed gasification, and potassium metal has been detected in the gas phase at gasification

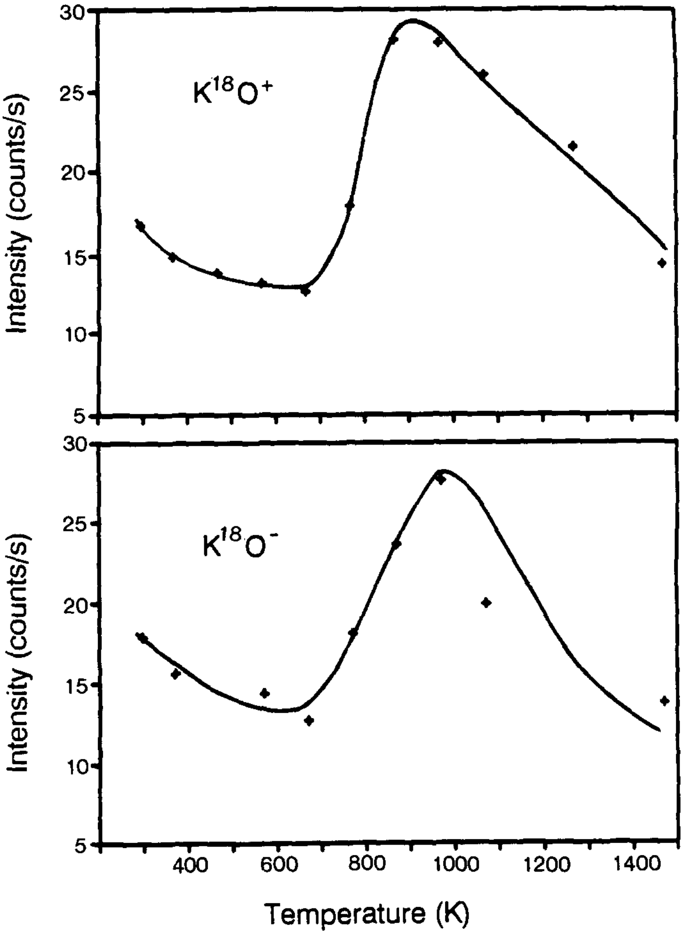


FIG. 4. Temperature dependence of the $K^{18}O^+$ and $K^{18}O^-$ secondary ion signals for the $K_2C^{18}O_3$/^{13}C mixture. Standard deviations of the $K^{18}O^-$ and $K^{16}O^-$ signals are 15 and 15%, respectively.

temperatures (1000–1200 K) by Knudsen cell mass spectrometry (*8*). Although the appearance of gas-phase potassium metal has led some workers (*28*, *29*) to propose that metallic potassium may be a surface intermediate in gasification, the similarity in temperature of K_2O decomposition and K metal detection suggests that K metal formation is limited by K_2O decomposition.

The invariance of the $K_2^{18}O^+$ and $K_2^{16}O^+$ intensities from 300 to 800 K (Fig. 3b) suggests that the carbonate does not thermally decompose below 800 K. Saber *et al.* (*25*) also reported that most of the $^{13}CO_2$ in the TPD spectrum of the $K_2^{13}CO_3$/carbon black mixture (Fig. 3a) between 550 and 1000 K was due to isotope exchange between the carbonate and $^{12}CO_2$ derived from surface oxides on the carbon and was not due to carbonate decomposition.

Unlike K_2O^+, the intensities of $K^{18}O^+$ and $K^{18}O^-$ ions decrease as the temperature increases from 300 to 700 K (Fig. 4). Above 700 K, the $K^{18}O^+$ and $K^{18}O^-$ intensities then increase to a maximum at about 950 K and subsequently decrease again above 1000 K. The $K^{16}O^+$ and $K^{16}O^-$ signals exhibit essentially the same temperature variations as the $K^{18}O^+$ and $K^{18}O^-$ signals.

Variations in ion intensities due to changes in the electronic properties of surfaces generally cause positive and negative ion intensities to change in opposite directions. The similar intensity variations exhibited by the KO^+ and KO^- ions indicate that the intensity variations of these ions are dominated by changes in the concentrations of the surface species that contribute to these ions as opposed to variations in the electronic properties of the surface.

Thus, if the KO^+ and KO^- ions are derived in part by fragmentation of surface K_2O species and in part by recombination processes involving oxygen derived from surface water, as suggested above, then the intensity variations of these ions should reflect changes in the surface concentrations of both K_2O and H_2O. A comparison of Fig. 4 with the intensity variations of the K_2O^+ ions in Fig. 3b and the H_2O^+ ions in Fig. 2 shows that the KO^+ and KO^- ion intensities reflect changes in the surface concentrations of both K_2O and H_2O. The decrease in the KO^+ and KO^- intensities for increasing temperatures between 300 and 700 K correlates with the desorption of water indicated in Fig. 2. The increase in the KO^+ and KO^- intensities between 700 and 950 K, on the other hand, correlates with changes in the surface concentration of K_2O. The shift in the peak maximum of the KO^+ and KO^- curves to slightly lower temperatures than the K_2O^+ curve in Fig. 3b can be accounted for by the contribution to the KO^+ and KO^- intensities of surface water, which desorbs in this temperature range (Fig. 2).

The strong correlation of the KO^+ and KO^- ion intensities to changes in the surface concentrations of both K_2O and H_2O strongly supports the interpretation that the KO^+ and KO^- ions are derived in part by fragmentation of surface K_2O species and in part by recombination processes involving surface water. The constant K_2O^+ intensity between 300 and 800 K also shows

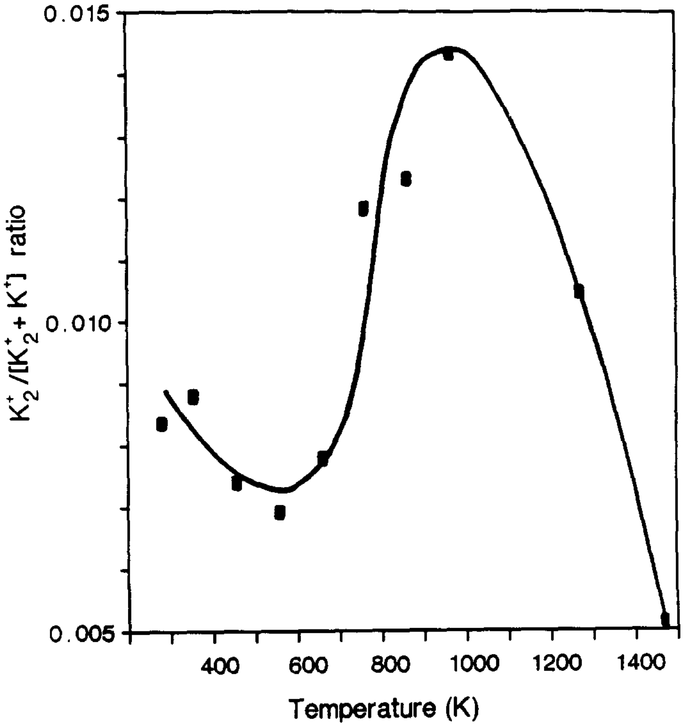


FIG. 5. Temperature dependence of the $K_2^+/(K^+ + K_2^+)$ ion intensity ratio for the $K_2C^{18}O_3/^{13}C$ mixture. Standard deviation of the $K_2^+/(K_2^+ + K^+)$ ratio is 10%.

that K_2O^+ ions are not derived by recombination processes involving surface water, since the surface concentration of water decreases in this temperature range.

Also of interest is the variation with temperature of the $K_2^+/(K_2^+ + K^+)$ ratio, which is the fraction of potassium ions that eject as dimers. As seen from Fig. 5, the $K_2^+/(K_2^+ + K^+)$ ratio exhibits a variation with temperature similar to the K_2O^+ intensity. This suggests that the K_2^+ and the K_2O^+ ions are derived from the K_2O surface species. Since the formation of K_2^+ requires close proximity between two K atoms on the surface, the K_2^+ ions are apparently derived primarily from K atoms associated with the same K_2O molecule. In contrast, for the $Ca^{13}CO_3/^{12}C$ system (*30*), CaO^+ ions appear in the SIMS spectrum following thermal treatment, but neither Ca_2^+ nor Ca_2O^+ ions were observed. This suggests that $CaCO_3$ thermally decomposes to CaO, and, in the absence of Ca_2O species, Ca atoms are not sufficiently close together to form Ca_2^+ ions.

CONCLUSIONS

Using secondary ion mass spectrometry, we have examined the interaction of K_2CO_3 with carbon black before and after thermal treatments. The results suggest that K_2CO_3 decomposes above 800 K to form K_2O. The K_2O subsequently decomposes above 1070 K, apparently forming metallic potassium, which either vaporizes or diffuses into the bulk. The water initially contained in the sample mixture appears to interact with some of the carbonate at 300 K to form K_2O and ^{18}O-labeled water.

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