

**Lateral interaction effects on the reaction of CO<sub>2</sub> and oxygen adsorbed on Ag(110)**

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# Lateral interaction effects on the reaction of CO<sub>2</sub> and oxygen adsorbed on Ag(110)

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The effect of oxygen adatom coverage and order upon the formation of CO<sub>3</sub> intermediates via CO<sub>2</sub> + O(a) → CO<sub>3</sub>(a) was examined on the Ag(110) surface. The reaction probability for CO<sub>2</sub> was found to be strongly dependent upon the oxygen adlayer. Adsorption of CO<sub>2</sub> upon an ordered oxygen adlayer at 300 K occurred with a net reaction probability of the order of 10<sup>-2</sup> or less, and resulted in the formation of (1×2) domains of CO<sub>3</sub> which caused compression of the adsorbed (n×1) oxygen atom chains as determined by LEED experiments. Adsorption of CO<sub>2</sub> upon a disordered oxygen adlayer at 170 K occurred with an initial sticking probability of unity; however, the saturation coverage of CO<sub>3</sub> intermediates formed was less than the initial oxygen atom coverage. Adsorption of CO<sub>2</sub> upon an ordered oxygen adlayer at 170 K occurred with lower reaction probability than at 300 K, indicating that the order of the oxygen adlayer strongly affected the CO<sub>2</sub> reaction kinetics. In all cases the reaction of CO<sub>2</sub> was hindered by increasing the initial oxygen atom coverage.

## INTRODUCTION

The formation of surface carbonate intermediates on the Ag(110) surface via

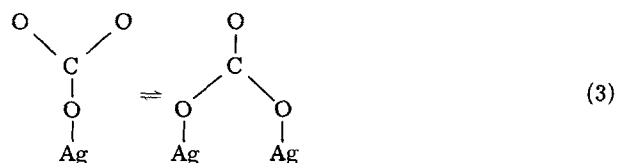


was recently demonstrated by Bowker *et al.*<sup>1</sup> This reaction may be characterized as a Lewis acid-base association between the Lewis acid (electron acceptor) CO<sub>2</sub> and the Lewis base (electron donor) O(a). Bowker *et al.*<sup>1</sup> showed that for initial oxygen coverages of the order of 10% of a monolayer, the adsorbed oxygen atoms could be saturated with CO<sub>2</sub> on a 1:1 basis to form CO<sub>3</sub>(a). Upon heating, Reaction (1) above was reversed to yield CO<sub>2</sub> in a first order process at 485 K with a rate of the form<sup>1</sup>

$$r_{\text{CO}_2} = 10^{13} \text{s}^{-1} \exp(-115 \text{ kJ mol}^{-1}/RT) [\text{CO}_3(a)] \quad (2)$$

The oxygen atoms released upon decomposition of the CO<sub>3</sub> species recombined and desorbed at 590 K<sup>1</sup> as also observed for the recombination of oxygen atoms following oxygen adsorption.<sup>2</sup> As CO<sub>2</sub> does not exhibit a stable adsorption state above 150 K on silver, the CO<sub>2</sub> evolved at 485 K was equal to the coverage of adsorbed carbonates formed.<sup>1</sup>

The reaction of CO<sub>2</sub> with adsorbed <sup>18</sup>O atoms was used by Bowker *et al.*<sup>1</sup> to demonstrate that the three oxygen atoms on the CO<sub>3</sub> species were statistically equivalent. Following the formation of C<sup>16</sup>O<sup>16</sup>O<sup>18</sup>O species by reaction of CO<sub>2</sub> with <sup>18</sup>O(a), the isotopic ratios of the decomposition products were approximately C<sup>16</sup>O<sub>2</sub>/C<sup>16</sup>O<sup>18</sup>O = 1/2, and <sup>18</sup>O/<sup>16</sup>O = 1/2, indicating that the oxygen initially adsorbed on the surface became indistinguishable from that contained in the adsorbing CO<sub>2</sub>.<sup>1</sup> It was therefore suggested<sup>1</sup> that this statistical equivalence of the oxygen atoms was achieved by facile interconversion of monodentate and bidentate intermediates



proposed by Force and Bell<sup>3</sup> on the basis of IR data.

In contrast to the low coverage, single crystal study of Bowker *et al.*<sup>1</sup> previous studies<sup>4-8</sup> of the interaction of CO<sub>2</sub> with oxygen adsorbed on silver powders have reported only partial saturation of adsorbed oxygen with CO<sub>2</sub>. Studies of the oxidation of CO<sup>4,9,10</sup> have also reported incomplete removal of adsorbed oxygen by CO, and it was suggested by Bowker *et al.*<sup>1</sup> that this effect might be due to the readsorption of the product CO<sub>2</sub> to form stable adsorbed carbonates. A similar suggestion was made<sup>1</sup> for anomalous LEED behavior reported in one study<sup>11</sup> for the adsorption of oxygen on Ag(110) and attributed<sup>12</sup> to a CO-oxygen interaction on the surface.

In order to clarify the differences between the above studies, we have examined the reaction of CO<sub>2</sub> with adsorbed oxygen atoms as a function of surface coverage and the ordering of the adsorbed layer. It will be shown that the "CO-oxygen interaction behavior" of Engelhardt *et al.*<sup>12</sup> is indeed due to the formation of surface carbonates, and that strong interactions between adsorbed CO<sub>3</sub>(a) and O(a) species may prevent saturation of the oxygen adlayer with CO<sub>2</sub>.

## EXPERIMENTAL

The experimental apparatus has been described in detail elsewhere.<sup>1</sup> Oxygen and CO<sub>2</sub> were dosed sequentially onto the surface through separate stainless steel needles and leak valves. This technique resulted in approximately a two order of magnitude enhancement of the effective pressure at the surface during exposure which is reflected in the exposures reported. Thermal desorption products were monitored with a UTI 100 C mass spectrometer which was multiplexed with a PDP-11 computer in order to monitor the CO<sub>2</sub> and O<sub>2</sub> products simultaneously.

## RESULTS

The formation of surface carbonate species by reaction of CO<sub>2</sub> with O(a) on the Ag(110) surface was found to be strongly dependent upon the ordering of both O(a) and CO<sub>3</sub>(a) species on the surface. The results are grouped

below with respect to the ordering of adsorbed surface species.

#### A. O<sub>2</sub>, CO<sub>2</sub> adsorbed at 300 K

The adsorption of oxygen on the Ag(110) surface at 300 K results in the observation of a series of ( $n \times 1$ ) ( $n = 7, 6, \dots, 2$ ) LEED patterns depending upon the surface coverage, as previously reported.<sup>2</sup> These surface



FIG. 1. LEED patterns observed following exposure of the Ag(110) surface to 600 L O<sub>2</sub> followed by CO<sub>2</sub> at 300 K: (a) CO<sub>2</sub> exposure = 240 L, beam energy = 45 eV. (b) CO<sub>2</sub> exposure = 600 L, beam energy = 35 eV. (c)  $p(3 \times 1)$  oxygen LEED pattern following heating of the surface in (b) to 520 K to decompose CO<sub>3</sub> species, beam energy = 46 eV.

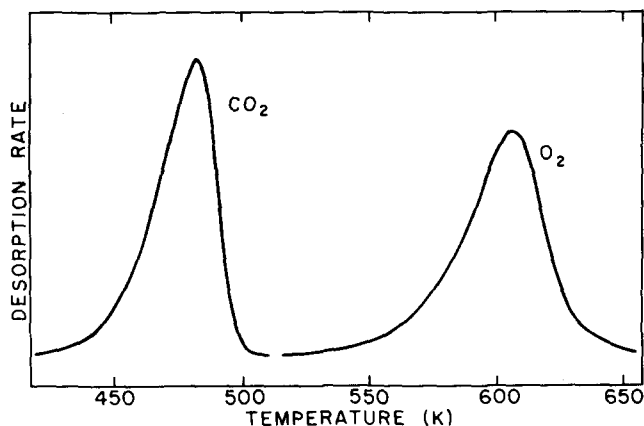


FIG. 2. Thermal desorption spectrum following exposure of the Ag(110) surface to 600 L O<sub>2</sub> + 240 L CO<sub>2</sub> at 300 K.

oxygen structures are due to the formation of chains of oxygen atoms along the (001) direction on the surface which interact repulsively along the (1 $\bar{1}$ 0) direction.<sup>2</sup> The adsorption of CO<sub>2</sub> on such a surface resulted in the formation of ordered CO<sub>3</sub>(a) structures which showed clear evidence of interaction with the unreacted adsorbed oxygen.

The additional features in the LEED patterns due to CO<sub>3</sub> formation at 300 K showed  $p(1 \times 2)$  symmetry. Figure 1 shows the LEED patterns observed for reaction of CO<sub>2</sub> with approximately  $\frac{1}{3}$  monolayer of oxygen atoms. When the oxygen atoms were partially consumed, the LEED pattern was a superimposition of a  $p(2 \times 1)$  due to unreacted oxygen atoms and a  $p(1 \times 2)$  due to CO<sub>3</sub> species [Fig. 1(a)]. As the exposure to CO<sub>2</sub> was increased, the coverage of CO<sub>3</sub> increased and that of unreacted oxygen decreased, thus the (1 $\times$ 2) LEED features were enhanced at the expense of the (2 $\times$ 1) [Fig. 1(b)]. The formation of CO<sub>3</sub> species may be reversed by heating, and the LEED pattern returned to that for adsorbed oxygen upon heating to 520 K to decompose the CO<sub>3</sub> [Fig. 1(c)]. A typical desorption spectrum for decomposition of surface carbonate is shown in Fig. 2.

It is clear that in order to form CO<sub>3</sub> structures of different geometry than the adsorbed oxygen atoms, the oxygen atom chains must be disrupted, and the attractive interactions between the oxygen atoms in the (001) direction overcome. In addition the formation of (2 $\times$ 1) oxygen features in the LEED pattern from an initially less densely packed oxygen structure (3 $\times$ 1) indicated that the formation of surface carbonates compressed the oxygen remaining on the surface, i.e., the perpendicular domains of CO<sub>3</sub>(a) and O(a) interacted repulsively. These interactions were further demonstrated by the dependence of the CO<sub>3</sub> coverage vs CO<sub>2</sub> exposure behavior upon the initial oxygen coverage.

As the formation of (1 $\times$ 2) domains of surface carbonate intermediates caused compression of the remaining ( $n \times 1$ ) oxygen chains into structures of lower  $n$ , one would expect the formation of surface carbonates to be more difficult for high initial oxygen coverages at which the oxygen atom chains are already in close proximity, with little freedom for additional compression. Such

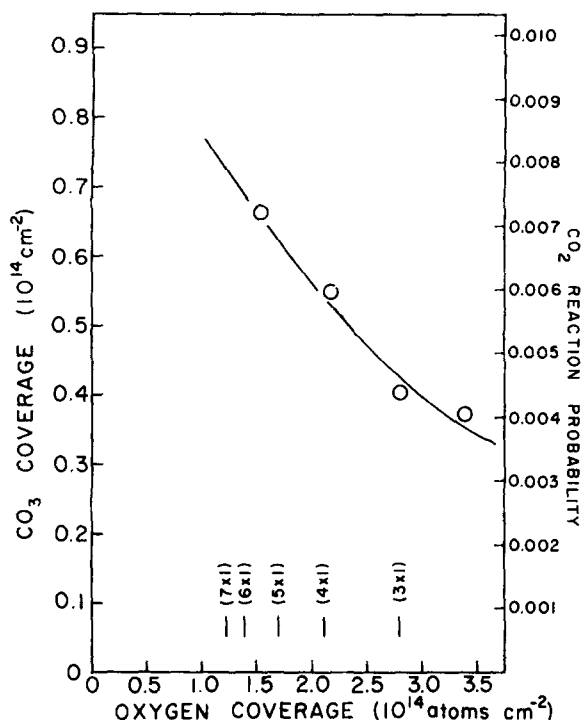


FIG. 3. Effect of initial oxygen coverage upon CO<sub>3</sub> formation at 300 K. CO<sub>2</sub> exposure = 30 L.

behavior was indeed observed for the reaction of CO<sub>2</sub> with oxygen adlayers of different coverage at 300 K. As shown in Fig. 3, for a constant exposure of CO<sub>2</sub> (30 L) the coverage of surface carbonates formed *decreased* as the initial surface oxygen coverage was increased. Thus the initial reaction probability for CO<sub>2</sub> exhibited a negative order dependence upon the surface oxygen atom concentration due to repulsive interactions between the (1×2) domains of carbonate formed and the oxygen ad-atom chains.

The reaction probability for CO<sub>2</sub> also decreased as the concentration of surface carbonates was increased. As shown in Fig. 4 for the reaction of CO<sub>2</sub> with about

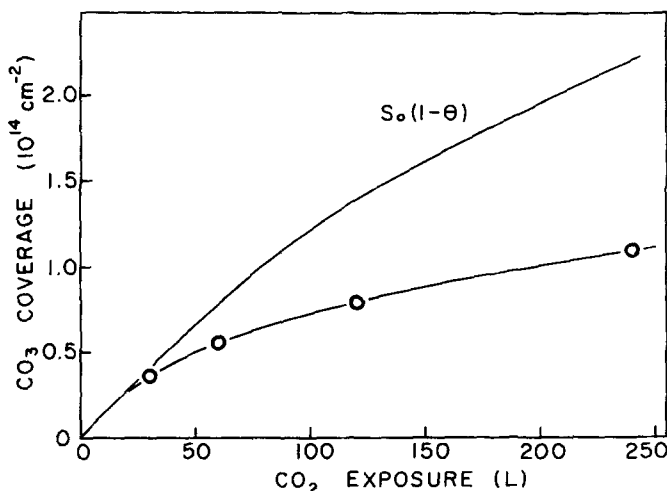


FIG. 4. Comparison of CO<sub>2</sub> adsorption profile at 300 K with Langmuir  $s_0(1-\theta)$  model.  $\theta(a) = 3.4 \times 10^{14}$  atoms cm<sup>-2</sup>.  $s_0 = 4.4 \times 10^{-3}$ .

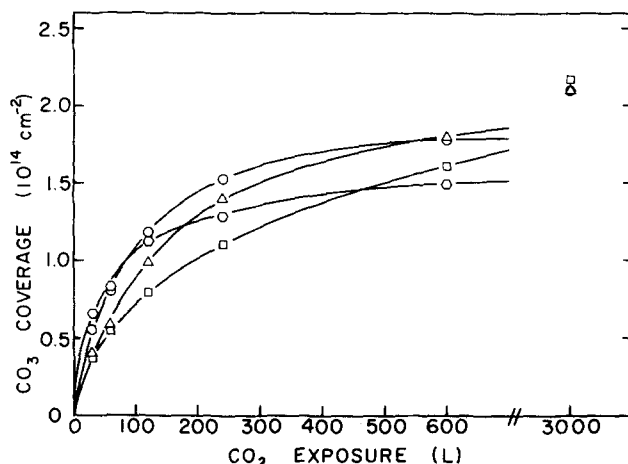


FIG. 5. CO<sub>3</sub> coverage vs CO<sub>2</sub> exposure profiles at varying initial oxygen coverages. Adsorption temperature for O<sub>2</sub> and CO<sub>2</sub> = 300 K.  $\circ$  exposure = 120 L,  $\theta_{O(a)} = 1.5 \times 10^{14}$  atoms cm<sup>-2</sup>.  $\circ$  exposure = 240 L,  $\theta_{O(a)} = 2.1 \times 10^{14}$  atoms cm<sup>-2</sup>.  $\Delta$  exposure = 600 L,  $\theta_{O(a)} = 2.8 \times 10^{14}$  atoms cm<sup>-2</sup>.  $\square$  exposure = 1800 L,  $\theta_{O(a)} = 3.4 \times 10^{14}$  atoms cm<sup>-2</sup>.

40% of a monolayer of O atoms, this falloff in the reaction probability was much larger than the Langmuir  $(1-\theta)$  dependence expected due to consumption of oxygen atoms. This result again suggested the repulsive interactions between the domains of CO<sub>3</sub>(a) and O(a) on the surface: as the CO<sub>3</sub> coverage was increased the local concentration of oxygen atom chains was increased due to compression, and the reaction probability for CO<sub>2</sub> declined. Thus the effect of high local oxygen atom coverages upon the reaction probability for CO<sub>2</sub> was similar to that for high initial coverages of oxygen which covered the entire surface. CO<sub>3</sub> coverage vs CO<sub>2</sub> exposure profiles are shown for several initial oxygen coverages in Fig. 5. For the curves at initial oxygen coverages of less than one-quarter monolayer the initial reaction probability was higher, and nearly all of the adsorbed oxygen reacted at CO<sub>2</sub> exposures of 600 to 3000 L. At higher initial oxygen coverages a significant fraction of adsorbed oxygen atoms was not saturated with CO<sub>2</sub> at exposures of 3000 L.

## B. O<sub>2</sub>, CO<sub>2</sub> adsorbed at 170 K

Oxygen adsorbed on the Ag(110) surface at 170 K is arranged randomly on the surface. No ordered LEED patterns are observed for up to 0.5 monolayers of oxygen atoms adsorbed under these conditions.<sup>13</sup> This result, as well as the CO oxidation-LEED work of Albers *et al.*<sup>14</sup> suggests that oxygen atoms are essentially immobile on the surface below 300 K. Similar conclusions for organic intermediates also appear to be supported by LEED-thermal desorption studies on the Ag(110) surface.<sup>15</sup> Thus by adsorbing O<sub>2</sub> and CO<sub>2</sub> at 170 K, both the barrier to disruption of ordered O(a) structures by CO<sub>2</sub> and the repulsive interactions between ordered domains of O(a) and CO<sub>3</sub>(a) may be eliminated.

As might be expected due to the appreciable differences in the ordering of the adsorbed layer at 170 K, the CO<sub>2</sub> adsorption behavior at 170 K differed appreci-

ably from that at 300 K. At 300 K the initial reaction probability for CO<sub>2</sub> was of the order of 10<sup>-2</sup> or less, and declined more rapidly than predicted by a Langmuir isotherm. At 170 K the sticking probability for CO<sub>2</sub> was unity up to CO<sub>3</sub> coverages of the order of one-third of the initial oxygen atom coverage. At higher exposures of CO<sub>2</sub>, however, the CO<sub>3</sub> coverage vs CO<sub>2</sub> exposure profile was quite flat, and indeed the saturation coverage of CO<sub>3</sub> decreased as the initial oxygen coverage was increased. This behavior is illustrated in Fig. 6. These results may be easily explained in terms of the lack of ordering of the adsorbed layer at 170 K. For isolated oxygen atoms, one would expect the reaction probability to be quite high, as no rearrangement of the adlayer is necessitated by the reaction, and the corresponding entropy and enthalpy barriers to rearrangement may be neglected. However at the oxygen coverages of Fig. 6 (of the order of  $\frac{1}{4}$ – $\frac{1}{3}$  monolayer), a significant number of oxygen atoms may be adsorbed in adjacent sites on the surface. If one assumes that the ordering of CO<sub>3</sub> species at 300 K is favored at least in part by repulsive interactions between the CO<sub>3</sub>(a) species, the lack of ordering at low temperature may prevent the reaction of CO<sub>2</sub> with oxygen atoms if the oxygen atoms are adsorbed in a configuration which would be unfavorable for the product carbonates. Thus for adsorption of O<sub>2</sub> and CO<sub>2</sub> at 170 K, CO<sub>2</sub> reacted with high probability with the "available" oxygen atoms, however all of the adsorbed oxygen could not be saturated with CO<sub>2</sub>.

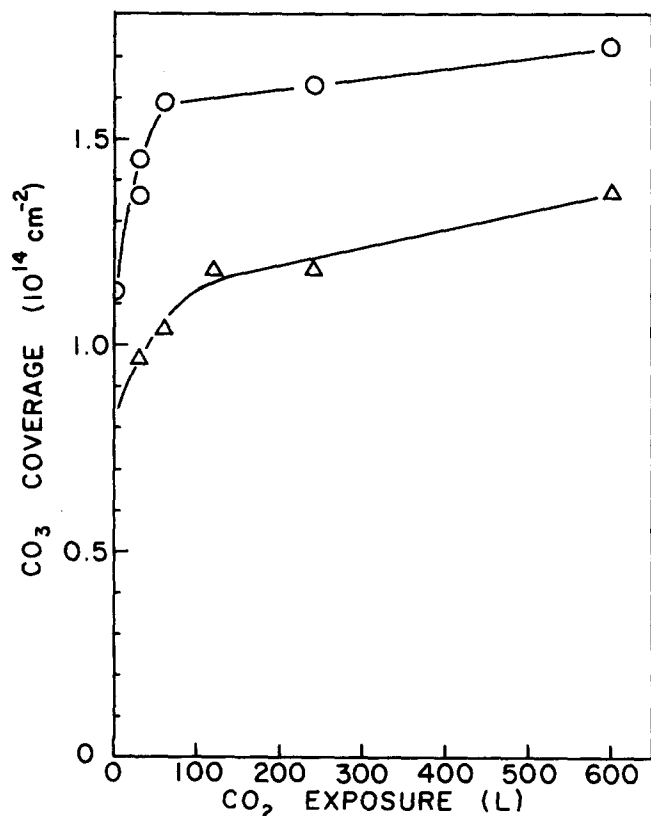


FIG. 6. CO<sub>3</sub> coverage vs CO<sub>2</sub> exposure profiles at varying initial oxygen coverages. Adsorption temperature for O<sub>2</sub> and CO<sub>2</sub> = 170 K. ○ exposure = 240 L,  $\theta_{O(a)} = 2.1 \times 10^{14}$  atoms cm<sup>-2</sup>. Δ exposure = 600 L,  $\theta_{O(a)} = 2.8 \times 10^{14}$  atoms cm<sup>-2</sup>.

TABLE I. CO<sub>3</sub> formed by exposure of  $2.1 \times 10^{14}$  atoms cm<sup>-2</sup> of O(a) to 30 L CO<sub>2</sub>.

Adsorption Temperature (K)		CO <sub>3</sub> coverage ( $\pm 0.1$ ) $\times 10^{13}$ cm <sup>-2</sup>
O <sub>2</sub>	CO <sub>2</sub>	
300	300	5.5
300	170	1.7
170	170	14.5

### C. Oxygen adsorbed at 300 K, CO<sub>2</sub> at 170 K

If one were unaware of the differences in the ordering of the oxygen adlayer at 170 and 300 K, the above data would suggest that CO<sub>3</sub> formation was more facile at 170 K, and that the apparent activation energy for CO<sub>2</sub> oxidation would be negative. In order to make a valid comparison, however, it is necessary to conduct the reaction under the same initial surface conditions. Several experiments were conducted in which oxygen was adsorbed on the surface at 300 K to form an ordered adlayer, and the surface was cooled to 170 K before exposure to CO<sub>2</sub>. Extensive coverage vs exposure profiles were not determined under these conditions, however, as shown in Table I, the coverage of CO<sub>3</sub> was reduced significantly when the adsorption temperature was lowered. These results show that the reaction of CO<sub>2</sub> with an ordered oxygen adlayer is, indeed, an activated process. Further, the difference in the initial reaction probability for CO<sub>2</sub> at 170 K of two to three orders of magnitude depending upon the arrangement of surface oxygen atoms demonstrates the profound effect that the distribution of surface species may have upon adsorption kinetics.

## DISCUSSION

In view of the strong dependence of the kinetics of CO<sub>2</sub> adsorption upon the coverage and distribution of the adsorbed oxygen atoms, the multitude of conflicting results reported previously<sup>1,4-8</sup> is, perhaps, not surprising. It has been reported that CO<sub>2</sub> cannot be adsorbed on top of a saturated oxygen adlayer,<sup>8</sup> that partial saturation of adsorbed oxygen with CO<sub>2</sub> is possible,<sup>4,5,7</sup> and finally, that CO<sub>2</sub> may be adsorbed in a 1:1 correspondence with the number of adsorbed oxygen atoms.<sup>1,6</sup> All but one of these studies<sup>1</sup> were conducted on silver powders, thus information on the ordering of adsorbed species from single crystal work cannot be applied directly to these studies. However as all of the previous studies were conducted at 273 K and above, it is reasonable to assume that the adsorbed oxygen species were indeed ordered. The studies which report partial saturation of the oxygen adlayer with CO<sub>2</sub> are in qualitative agreement with the present study. Of the two studies which reported complete saturation of oxygen atoms, one<sup>1</sup> involved oxygen coverages of about 10% of a monolayer, which as shown can be easily saturated with CO<sub>2</sub>, and the other<sup>6</sup> assumed that only a fraction of the total oxygen coverage was atomically adsorbed and the CO<sub>2</sub> uptake was related to this fraction. The work of Keulks and Chang<sup>8</sup> is perhaps the most difficult to explain. These authors reported no isotopic exchange between C<sup>16</sup>O<sup>18</sup>O and a surface saturated with <sup>16</sup>O atoms. At

lower oxygen coverages, however, substantial exchange was observed.<sup>8</sup> In the present study CO<sub>2</sub> was observed to react with adsorbed oxygen up to initial oxygen atom coverages of 0.5 monolayer. At higher oxygen coverages oxygen adsorption on silver powders has been reported to be molecular<sup>16-18</sup> and CO<sub>2</sub> does not appear to interact with molecularly adsorbed oxygen.<sup>13</sup> In general, however, the lack of complete saturation of adsorbed oxygen with CO<sub>2</sub> and the incomplete equilibration of oxygen isotopes between the reactants in previous studies are not indicative of the stoichiometry of the surface intermediates formed: experiments in which adsorbed oxygen was completely reacted show that the only intermediate formed is CO<sub>3</sub>(a).<sup>1</sup> Rather these results demonstrate the strong interactions which occur between adsorbed CO<sub>3</sub> and O species, even when the surfaces studied are not well defined.

The results of this study also show that the anomalous LEED effects for oxygen adsorption on Ag(110) reported by Bradshaw *et al.*<sup>11</sup> were due to the formation of small amounts of surface carbonate intermediates. Engelhardt *et al.*<sup>12</sup> previously showed that the contamination of the oxygen dosed onto the surface with small amounts of CO led to irreversible changes in the work function which were attributed to a CO-oxygen interaction on the surface. It was suggested<sup>12</sup> that such interactions might explain the anomalies in the previous study.<sup>11</sup> Bowker *et al.*<sup>1</sup> suggested that this CO-oxygen interaction was, in fact, the formation of surface carbonates by the further oxidation of the CO<sub>2</sub> produced by CO oxidation. However the additional LEED features [*p*(1×2) structure, broadening of the *p*(2×1) oxygen features] reported by Bradshaw<sup>11</sup> have not previously been accounted for. As shown in Fig. 1(a), these additional features are precisely those observed for partial reaction of the oxygen adlayer with CO<sub>2</sub> to form adsorbed carbonates. Thus the conclusion of Bowker *et al.*<sup>1</sup> that the irreversible work function changes reported by Engelhardt *et al.*<sup>12</sup> and the incomplete removal of oxygen atoms during CO oxidation<sup>4,9,10</sup> were due to surface carbonate formation appear to be supported by the present data.

The interactions between the ordered CO<sub>3</sub> and oxygen structures observed in this study are rather remarkable. The formation of (1×2) domains of carbonate from (*n*×1) oxygen structures requires a large scale rearrangement of the adsorbed layer, including the movement of adsorbed species across the ridges of the (110) surface. The attractive interactions between the unreacted oxygen atoms were apparently sufficient to prevent the oxygen atoms from "spreading out" along the alternate troughs not occupied by CO<sub>3</sub> species in the (1×2) structure. Thus the repulsive interactions between CO<sub>3</sub>(a) and O(a) species cause the formation of perpendicular domains which appear to enclose large vacant areas on the surface. This behavior is illustrated schematically in Fig. 7. LEED patterns of comparable intensity to Fig. 1(a) were observed for partial saturation of initial oxygen coverages as low as  $\frac{1}{4}$  monolayer. (Below this coverage the additional LEED features were less intense and less well defined.) Assuming approximately equal coverages of CO<sub>3</sub> and O species for equal intensity (1×2) and (2×1) structure, coverages as low

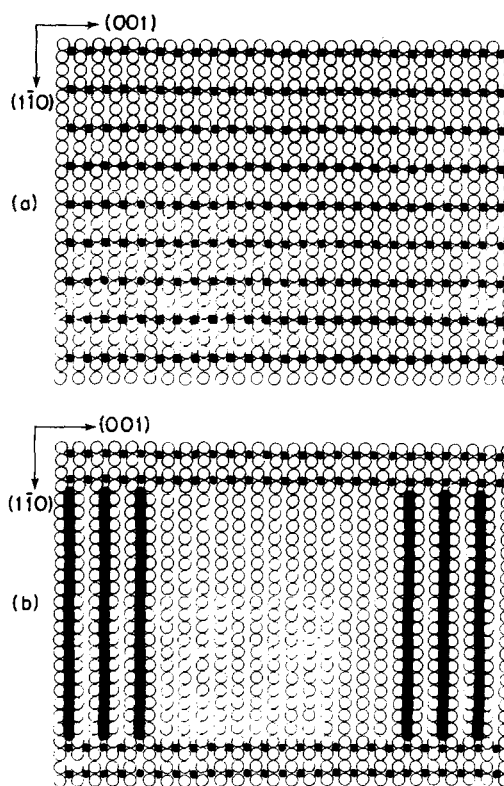


FIG. 7. (a) Adsorbed oxygen layer which produces a  $p(3 \times 1)$  LEED pattern. (b) A schematic illustration of the perpendicular domains of CO<sub>3</sub>(a) + O(a) and the creation of vacant areas on the surface. The concentration of adsorbed species [CO<sub>3</sub>(a) + O(a)] is approximately equal to the concentration of oxygen atoms in (a). ○ Silver atoms on the ridges of the (110) surface. ● adsorbed oxygen atoms. ■ filled rows of CO<sub>3</sub>(a).

as  $\frac{1}{8}$  monolayer of each of the intermediates may therefore give rise to quite well defined LEED features suggestive of a local coverage of  $\frac{1}{2}$  monolayer. This suggests that in addition to the alternate vacant rows in the (1×2) and (2×1) structures, one half of the surface remains vacant and is enclosed by these dense domains. Such large scale segregation requires strong interactions between the adsorbed intermediates on the Ag(110) surface. These interactions are manifested in the strong dependence of the CO<sub>2</sub> reaction probability upon the ordering of surface oxygen atoms. The kinetics for decomposition of the CO<sub>3</sub>(a) species were unaffected by these interactions: Eq. (2) was found to apply independently of the coverages of CO<sub>3</sub>(a), O(a), or of the initial ordering of the adlayer.

## CONCLUSIONS

1. The reaction probability for the formation of surface carbonate intermediates via CO<sub>2</sub> + O(a) → CO<sub>3</sub>(a) is strongly dependent upon the ordering of the oxygen adlayer initially adsorbed.
2. If oxygen is adsorbed at 300 K, the oxygen adlayer is ordered in (*n*×1) chains. Reaction of adsorbed oxygen with CO<sub>2</sub> at 300 K results in the formation of (1×2) domains of adsorbed carbonate, and compression of the unreacted oxygen chains into a (2×1) structure.
3. If oxygen is adsorbed at 170 K, the oxygen adlayer

is disordered. Reaction with CO<sub>2</sub> at 170 K occurs with a reaction probability near unity up to a saturation CO<sub>3</sub> coverage which is less than the initial coverage of oxygen. The CO<sub>3</sub> saturation coverage falls as the oxygen coverage is increased due to the increasing proximity of adsorbed oxygen atoms and the immobility of CO<sub>3</sub>(a) and O(a) at this temperature.

4. The increase in the reaction probability of CO<sub>2</sub> at 170 K is due to the lack of order of the oxygen adlayer. The reaction probability for CO<sub>2</sub> with an ordered oxygen layer at 170 K is *less* than that at 300 K.

5. The surface intermediate formed by reaction of CO<sub>2</sub> with O(a) is CO<sub>3</sub> for all coverages of these species observed. Failure to saturate all of the adsorbed oxygen with CO<sub>2</sub> is indicative of strong repulsive interactions between these species, and not of the stoichiometry of the adsorbed intermediates.

#### ACKNOWLEDGMENTS

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