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Does CO₂ dissociatively adsorb on Cu surfaces?

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Abstract. The interactions of CO₂ with a clean Cu(110) surface have been studied both in an ultrahigh-vacuum surface analytical chamber and in an attached, high-pressure cell. No adsorption or dissociation of CO₂ was measured for exposures up to 350 L at 110 K and 250 K. Exposures of 65 to 650 Torr of CO₂ at 400–600 K led to the build-up of atomically adsorbed oxygen according to the reaction $\text{CO}_{2,g} \rightarrow \text{CO}_g + \text{O}_a$ at a rate which increased with temperature ($\sim 16 \text{ kcal mol}^{-1}$) and decreased with reaction time, saturating in a p(2 × 1)-O overlayer. The observed dissociative reaction probabilities for CO₂ of $\sim 10^{-9}$ – 10^{-11} (per collision with the surface) are favorably compared with predictions based upon the thermodynamics of adsorbed oxygen and the known kinetics of the reverse reaction: $\text{CO}_g + \text{O}_a \rightarrow \text{CO}_{2,g}$. The rates are also reasonably close to the reaction probability for CO₂ reported in the reverse water-gas shift reaction over Cu-based catalysts, which suggests a catalytic redox mechanism involving the dissociative adsorption of CO₂, followed by consumption of the resulting O_a by reaction with H₂. The results also show that CO₂:CO ratios in excess of ~ 100 would be required to produce significant oxygen concentrations on copper surfaces under catalytic methanol synthesis conditions. We were unable to produce surface carbonate from O_a plus CO₂ on Cu(110).

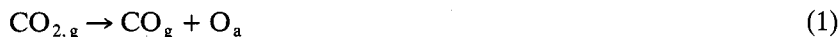
1. Introduction

There is some controversy in the literature concerning whether (or how fast) CO₂ dissociatively adsorbs on Cu surfaces to produce oxygen adatoms. In a recent study with a high-pressure cell attached to an ultrahigh-vacuum chamber, we found that the probability for producing oxygen adatoms by the dissociation of CO₂ on the Cu(111) surface ($\text{CO}_{2,g} \rightarrow \text{CO}_g + \text{O}_a$) was exceedingly small at 500 K (less than one reaction per 10⁶ collisions of CO₂ molecules with the surface) [1]. This was consistent with an earlier study by Habraken *et al* [2], who found no measurable interaction of CO₂ with Cu(111) in UHV. In sharp contrast, Wachs *et al* [3] mentioned in the appendix of an early paper that, on clean Cu(110), ‘greater than 99% of the adsorbed CO₂ molecules dissociated to CO and surface oxygen’ upon heating the surface after exposure at 180 K to CO₂. (Since the interaction of CO₂ was not the main point of that paper, no experimental details such as the CO₂ exposure or coverage were given.) Similarly, Copperthwaite *et al* [4] observed xps spectra after dosing CO₂ to polycrystalline Cu at 83 K and warming to 130 K, which they interpret as being due to partial dissociation of weakly adsorbed

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CO₂. Using radio-tracer and TPD methods, Hadden *et al* [5] recently concluded that CO₂ will dissociatively adsorb to produce oxygen adatoms on Cu powder via the reaction



From the time and temperature dependencies of the amount of CO evolution, they also concluded that a significant 'activation energy is associated with the process' but that 'the decomposition reaction is enhanced under low temperature conditions'. There are also a number of papers which interpret various experimental results over Cu powders [6] and supported Cu-based catalysts [6–11] in terms of dissociative CO₂ adsorption. In these studies, the CO₂ pressures were relatively high (>50 Torr) and no discussions of the rate of CO₂ dissociation were presented.

From a catalytic viewpoint, the rate of dissociative adsorption of CO₂ over Cu is very important. The methanol synthesis reaction ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$) over Cu–ZnO catalysts [6–11] (but not Cu–chromite catalysts [12]) is promoted by CO₂ addition to the feed. Some authors attribute this to the ability of CO₂ to adsorb dissociatively and therefore to maintain the proper coverage of O_a or surface oxide under reaction conditions [6–11]. Similarly, Hadden *et al* [5] argue that their observation of the mere existence of dissociative CO₂ adsorption on Cu 'demonstrates unequivocally that the reverse shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) is a sequential process, the initial step of which is decomposition of the carbon dioxide on the copper surface to give adsorbed carbon monoxide and a surface oxygen species, the latter then being scavenged by the hydrogen in the gas phase'. However, we believe that one can provide strong evidence in favour of this mechanism only by a careful comparison of the rate of CO₂ dissociation with the rate of the overall reverse shift reaction (under similar conditions of surface coverage). A careful measurement and thermodynamic estimation of the dissociative adsorption probability of CO₂ on copper is the main subject of this paper.

In this study we investigate the interactions of CO₂ with the clean Cu(110) surface both under ultrahigh vacuum and high-pressure dosing conditions. We find an exceedingly low reaction probability for the dissociative adsorption of CO₂ to produce oxygen adatoms (10^{-11} – 10^{-9} per collision). We also present a thermodynamic analysis which allows an estimate of the equilibrium surface coverage of O_a in CO₂–CO mixtures over Cu. Since the reaction probabilities for the reverse process



are well known over Cu(110) [13–14], we also use these thermodynamic results to calculate the expected dissociative adsorption probability for CO₂, and we compare this with our experimental results.

2. Experimental

The experiments were performed in an ultrahigh-vacuum (UHV) surface analytical chamber with an attached high-pressure cell and sample-transfer system very similar to one described previously [15]. The Cu(110) preparation and surface cleaning procedures are described elsewhere [16]. Surface cleanliness and long-range order were verified by AES and LEED respectively. The CO₂ was of SFC grade purity (~99.999%) with manufacturer-specified impurity levels of: <5 ppm of H₂, <5 ppm of CO, <2 ppm of O₂, <3 ppm of H₂O and <0.1 ppm organics. We also checked its purity with gas chromatography directly in our gas-handling system and could see no impurities (i.e.

< 3–10 ppm). For the micro-reactor volume (~40 ml) used in the high-pressure exposures here, a partial pressure of 10⁻³ Torr corresponds to about one monolayer on the Cu(110) surface (~1 cm²). Since CO₂ pressures of up to 650 Torr were required for high-pressure dosing, and since impurities of the order of a few ppm (~10⁻³ Torr) could not be prevented, we must consider the possibility that impurities in the gas phase could contribute to either deposition or clean-off of surface oxygen. The potential impurity sources for oxygen deposition would be O₂ or H₂O. Since we were only able to see observable deposition of O_a by using much higher-pressure doses of pure H₂O (~10 Torr) (i.e. the dissociative adsorption probability for H₂O is very low), we can rule out such problems due to H₂O. Since dissociative O₂ adsorption is relatively unactivated on Cu(110) [17], and since the build-up of oxygen we report here is highly activated (see below), we can rule out problems due to O₂. The possible sources for removal of O_a are H₂ and CO. Since the reaction probability for clean-off by the reaction H₂ + O_a → H₂O is below ~3 × 10⁻⁷ per H₂ collision with the surface [26], the H₂ impurity here (<5 × 10⁻³ Torr) should not cause significant clean-off of oxygen during the time scale of our measurements. Since the reaction probability for clean-off by the reaction CO + O_a → CO₂ is below ~3 × 10⁻⁵ per CO collision with the surface [13], the CO impurity level here (<5 × 10⁻³ Torr) cannot quite be ruled out as a potential source for unwanted clean-off reactions. However, since we were able to drive the adsorbed oxygen coverage to full saturation ($\theta_0 = 0.5$) by dissociative CO₂ adsorption (see below), we can infer that any clean-off rate is slow compared to CO₂ dissociation, at least at low oxygen coverages.

The cleanliness of the gas-handling system, micro-reactor and sample-transfer system were verified by exposing the clean or oxygen-pre-dosed Cu(110) surface to 650–1000 Torr of N₂ for times of 1–7 minutes. Subsequent surface analysis showed no accumulation of surface impurities, and the initial coverage of O_a was not significantly changed during this N₂ exposure.

When dosing CO₂ at partial pressures near 65 Torr, N₂ gas at 650 Torr was also added together with the CO₂ to the high-pressure cell. This nitrogen buffer gas eliminated the slow build-up of carbon impurity. We assume this carbon came from the neighbouring differential pumping stage on the transfer rod, and that the flow of N₂ through the seals out of the high-pressure cell prevented back-streaming of carbon-bearing impurities.

3. Results

For CO₂ exposures up to 350 L to clean Cu(110) at 110 or 250 K, we were unable to adsorb any measurable amount of CO₂ or deposit any measurable amount of O_a (i.e. $\theta_0 < 0.03$) onto the surface, as evidenced by the complete lack of any measurable oxygen signal in Auger electron spectroscopy (AES) or x-ray photoelectron spectroscopy (XPS). No other impurities appeared on the surface following these exposures. These results show that the adsorption and reaction probabilities for CO₂ are less than 2 × 10⁻⁴ per collision of CO₂ molecules with the Cu(110) surface.

We also gave the clean Cu(100) surface exposures of CO₂ from 20 Torr up to 1300 Torr in the high-pressure cell at temperatures between 400 and 600 K and for times up to 10 min. The results at 650 Torr of CO₂ are presented in figure 1(a) as a function of sample temperature and reaction time. After exposure, the sample was transferred rapidly (<20 s) back into UHV. The surface oxygen concentration was then determined by measuring the O(KVV)/Cu(LVV) AES peak-to-peak ratio. This Auger ratio was

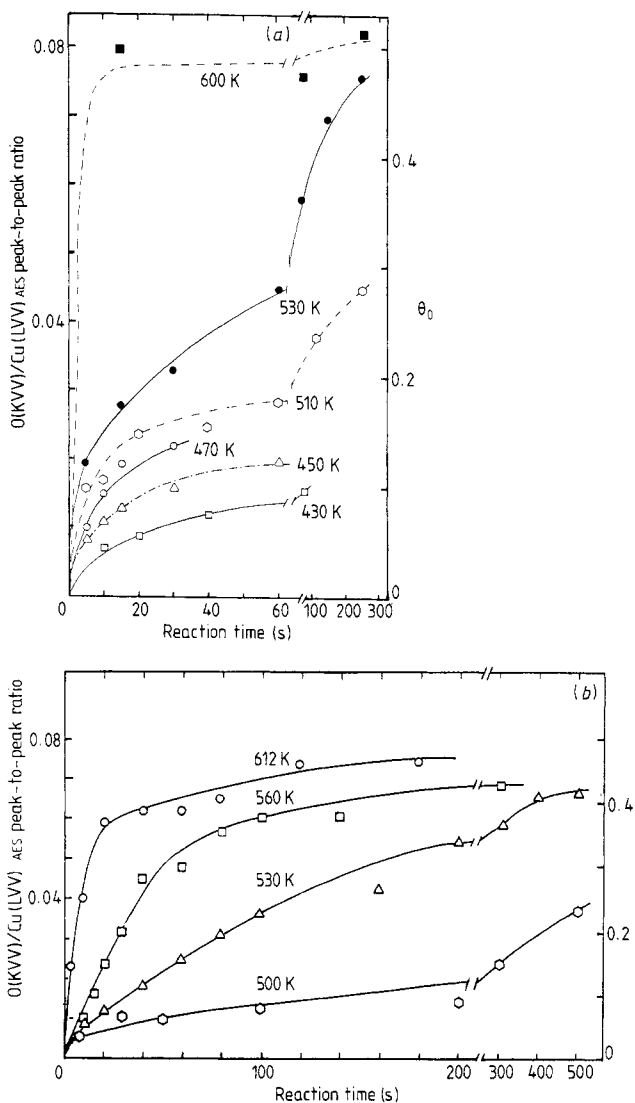
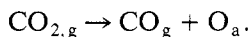


Figure 1. Oxygen coverage (as measured by the O/Cu AES ratio) versus reaction time for Cu(110) at various temperatures in (a) 650 Torr CO₂; (b) 65 Torr CO₂ + 650 Torr N₂.

scaled to absolute coverage units θ_0 using the ratio (0.08) measured in this same instrument for O₂ saturation exposure (~ 30 L) at 300 K on clean Cu(110), which is known to give an absolute oxygen coverage of 0.5 oxygen adatoms per Cu surface atom (i.e. $\theta_0 = 0.5$) [17]. The results in figure 1 indicate that the rate of CO₂ dissociation decreases with time (or oxygen coverage) and increases with temperature. Oxygen coverages up to $\theta_0 \approx 0.5$ were produced here with CO₂ exposures, but the surface reached saturation at about that point. This saturated adlayer showed a sharp $p(2 \times 1)$ LEED pattern identical to that seen for a saturated adlayer of oxygen adatoms ($\theta_0 = 0.5$) produced from dosing O₂ at room temperature in UHV [17]. Post-reaction analysis of the surface with AES indicated no measurable amount of other elements present on the surface. On the basis

of these results, we conclude that the product of the CO₂ exposures is a layer of oxygen adatoms (O_a). This implies that CO₂ dissociates on Cu(110) according to the net reaction



A similar mechanism (but with much higher probabilities) has been reported for CO₂ dissociation on Ni and Fe surfaces [18–19].

To test whether or not there was any consumption of O_a by background impurities during the CO₂ exposures or during transfer from the high-pressure cell to UHV, we also performed several experiments where we first dosed 6L O₂ to the surface at 300–600 K in UHV to produce a coverage of O_a of $\theta_0 \approx 0.5$. We then repeated the same type of 650 Torr CO₂ exposures as used on the clean surface and saw no measurable loss of the pre-dosed oxygen signal. In these control experiments, we of course chose CO₂ exposures such as 450 K for 60 s or 530 K for 20 s which, according to figure 1, would in themselves have led to much lower oxygen coverages than the pre-dosed amount. Thus these experiments show that the build-up of oxygen at low CO₂ exposures was not limited by severe clean-off reactions with some low-level impurities in the CO₂ gas.

We repeated experiments such as those shown in figure 1(a) at 530 K, only now we used 1300 Torr of CO₂. The build-up of O_a was approximately twice as fast as in figure 1(a), proving that the reaction rate is roughly first order with respect to CO₂ pressure. That is, the rate is proportional to the collision frequency of CO₂ molecules with the surface.

Similar experiments were also repeated at 65 Torr CO₂ and a variety of temperatures. These results are shown in figure 1(b). For $\theta_0 \leq 0.1$, the build-up of oxygen was approximately 10 times slower than at 650 Torr CO₂. Again, this shows that at low θ_0 the rate is nearly first-order with respect to P_{CO_2} . At higher θ_0 , the reaction order decreases to $\sim 0.7 \pm 0.1$.

Reaction probabilities for dissociative CO₂ adsorption to produce oxygen adatoms (per collision of CO₂ molecules with the surface) have been determined from the slopes of the uptake curves of figure 1. These are presented in Arrhenius form in figure 2. Here, we show probabilities obtained from the average slope for the coverage range $0 \leq \theta_0 \leq 0.1$, and from the instantaneous slope at an oxygen coverage $\theta_0 = 0.1$. As can be seen, the dissociative reaction probability falls in the range 10^{-11} – 10^{-9} over the temperature range 430–612 K, and the apparent activation energies are in the range 14.8–16.4 kcal mole⁻¹, depending on the coverage.

Hadden *et al* [5] observed the deposition of $\sim 18\%$ of a monolayer of O_a on polycrystalline Cu powder under 76 Torr CO₂ for 10 min at 498 K. As can be seen in figure 1(b), this is in good agreement with our present results for Cu(110). Since impurities are much less of a problem on such high-area samples, this agreement indicates that impurity clean-off reactions were not a problem in our present experiments.

Adsorbed carbonate is readily produced on some transition metal surfaces by the reaction $\text{CO}_2 + \text{O}_a \rightarrow \text{CO}_{3,a}$ [20]. In an attempt to synthesise carbonate on Cu(110), experiments were performed in which large exposures of CO₂ (650 Torr, up to 10 min) were given in the high-pressure cell to oxygen-covered ($\theta_0 \leq 0.25$) Cu(110) surfaces at 375 K. Post-reaction analysis of the surfaces with AES showed an increase in the amount of adsorbed oxygen, but not carbon. The line shape of the O(KVV) region was indistinguishable from that for atomic oxygen on Cu(110). Studies of the post-reaction surfaces with thermal desorption spectroscopy showed no evolution of CO₂. All these results suggest that under the examined conditions, carbonate was not formed in appreciable amounts on Cu(110).

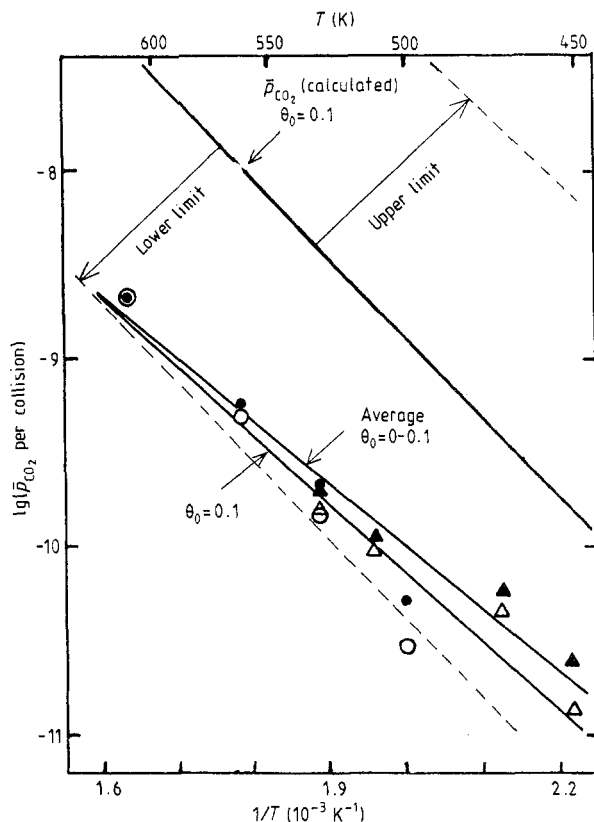


Figure 2. The dissociative adsorption probability for CO_2 (\bar{p}_{CO_2}) on Cu(110) versus temperature, plotted in Arrhenius form. The experimental data were determined from the slopes of the uptake curves of figure 1 taken at $\theta_0 = 0.1$ (open data points) and averaged over the range for θ_0 between 0 and 0.1 (full data points). The triangles are from figure 1(a) and the circles are from figure 1(b). The dotted lines are the lower and upper limits for \bar{p}_{CO_2} at $\theta_0 = 0.1$, calculated based on thermodynamic and kinetic considerations (see text).

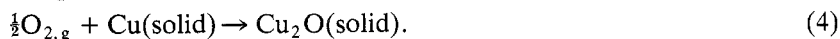
4. Discussion

It is useful to view the present results in the light of the thermodynamic driving force for dissociative CO_2 adsorption. Below, we will estimate this driving force and, from equilibrium considerations and a knowledge of the kinetics of the reverse reaction ($\text{CO}_{\text{g}} + \text{O}_{\text{a}} \rightarrow \text{CO}_{2,\text{g}}$), estimate the rate of dissociative CO_2 adsorption.

Let us first consider the simpler reaction:



where \square refers to a vacant site on the surface of solid Cu. Fortunately, the enthalpy for this latter reaction has been calorimetrically determined on polycrystalline Cu by separate groups to be $-(55.5 \pm 0.5)$ kcal mole $^{-1}$ of oxygen atoms near room temperature [21–22]. This compares with a value of -39.8 kcal mol $^{-1}$ at 298 K for the standard heat of formation of cuprous oxide [23]:



Since the major entropy for reactions such as (3) and (4) is mainly due to the loss of the

entropy associated with the translational and rotational degrees of freedom of the gaseous species, the entropy change for reaction (3) will be close to that for reaction (4) if oxygen adatoms are localised to specific lattice sites on Cu, as is indeed proven by LEED [17]. The accuracy of this statement can be seen by comparing the standard entropies of formation at 298 K of the solid oxides Cu₂O, CuO, CoO, Co₃O₄, FeO, Fe₃O₄, Fe₂O₃, MnO, Mn₃O₄, Mn₂O₃, MnO₂, MoO₂, NiO, Ag₂O and WO₂, all of which are (-19 ± 4) cal mol⁻¹ K⁻¹ (i.e., per mole of oxygen atoms), independent of the metal of choice [24]. We will therefore estimate the entropy change for reaction (3) as (-19 ± 4) cal mol⁻¹ K⁻¹. Combining this estimated entropy change with the known enthalpy for reaction (3) noted above, we can estimate the standard free energy change for that reaction:

$$\Delta G_3^0 = \Delta H_3^0 - T\Delta S_3^0 = -(55\,500 \pm 500) \text{ cal mol}^{-1} - T[-(19 \pm 4) \text{ cal mol}^{-1} \text{ K}^{-1}] \quad (5)$$

where T is temperature. At 298 K, equation (5) gives $\Delta G_3^0 = -(49.8 \pm 1.3)$ kcal mol⁻¹ for reaction (3). Since ΔH_3^0 and ΔS_3^0 are not very strongly dependent upon temperature, equation (5) should provide a satisfactory estimate of ΔG_3^0 (± 2 kcal mol⁻¹) over a temperature range from 298 to 600 K.

Now let us reconsider the related but more complex reaction involving surface oxidation of copper by CO₂:



where \square refers to a vacant surface site. Since the standard free energies for formation of both CO_{2,g} and CO_g have been tabulated as a function of temperature [23], and since we can use equation (5) above to estimate the free energy of formation of O_a on Cu, we can easily estimate the standard free energy change for reaction (6) as

$$\Delta G_6^0 = (12\,000 \pm 1000) \text{ cal mol}^{-1} - [(1.7 \pm 5) \text{ cal mol}^{-1} \text{ K}^{-1}] T. \quad (7)$$

Following the treatment of Kubsh and Dumesic [25], the equilibrium constant for reaction (6) can then be written as

$$K_6 = \frac{P_{\text{CO}}[O_a]}{P_{\text{CO}_2}[\square]} = \frac{P_{\text{CO}} \theta_0}{P_{\text{CO}_2} \theta_v} \quad (8)$$

where θ_0 and θ_v are the fractional coverages of oxygen adatoms and vacant surface sites respectively, and P_{CO_2} and P_{CO} are the partial pressures of CO₂ and CO respectively. (Here we have assumed unit activity coefficients.)

Using this relationship, we can now estimate the equilibrium constant for reaction (6) at low oxygen coverages (when $\theta_v \approx 1$) as

$$K_6 = \frac{P_{\text{CO}} \theta_0}{P_{\text{CO}_2}} = \exp(-\Delta G_6^0/RT) \quad (9)$$

where ΔG_6^0 can be determined from equation (7). Figure 3 shows the partial pressure ratio $P_{\text{CO}_2}/P_{\text{CO}}$ required to establish a coverage $\theta_0 = 0.1$ at equilibrium as a function of temperature, determined from equations (9) and (7). As can be seen, CO₂/CO ratios in excess of 10² are required to establish concentrations of O_a above 0.1 in the temperature range of interest in the methanol synthesis reaction (<600 K).

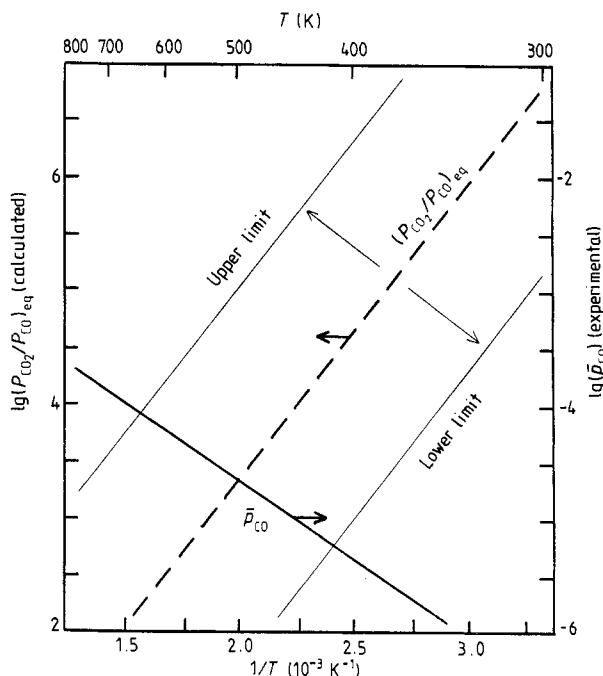


Figure 3. The temperature dependences of: (a) the CO_2/CO pressure ratio required to maintain an oxygen coverage of $\theta_0 = 0.1$ at equilibrium on Cu(110), calculated based on thermodynamic considerations (see text—estimated upper and lower limits of uncertainty are included); (b) the reaction probability for CO (\bar{p}_{CO}) in the reaction $\text{CO} + \text{O}_a \rightarrow \text{CO}_2$, determined experimentally at $\theta_0 = 0.25$ in [13].

Also shown in figure 3 is the experimentally determined reaction probability \bar{p}_{CO} for CO_g in the reverse reaction on the Cu(110) surface:



(Note that this overall reaction is thought to occur via adsorbed CO and a Langmuir–Hinshelwood mechanism [26].) The values for \bar{p}_{CO} plotted here are those from [13] for $\theta_0 = 0.25$. It should be noted that these values are within a factor of six on Cu(110), Cu(111) and Cu(100) [13], with the Cu(110) values toward the average. At equilibrium conditions, the O_a consumption rate by CO via reaction (10) must equal the O_a production rate by CO_2 via reaction (6), or

$$\bar{p}_{\text{CO}} P_{\text{CO}} = \bar{p}_{\text{CO}_2} P_{\text{CO}_2} \left(\frac{28}{44}\right)^{1/2} \quad (11)$$

where \bar{p}_{CO} and \bar{p}_{CO_2} represent the reaction probabilities of CO and CO_2 respectively, and the factor $(\frac{28}{44})^{1/2}$ is needed to convert partial pressures to (relative) collision frequencies. Thus, the equilibrium CO_2 reaction probability \bar{p}_{CO_2} according to reaction (6) can be estimated using the CO reaction probability \bar{p}_{CO} and the equilibrium CO_2 :CO pressure ratio from equations (7) and (9) or figure 3:

$$\bar{p}_{\text{CO}_2} = \left(\frac{28}{44}\right)^{1/2} \bar{p}_{\text{CO}} / (P_{\text{CO}_2}/P_{\text{CO}})_{\text{eq}}. \quad (12)$$

Since in a first approximation the CO reaction probability should be proportional to θ_0 , we have scaled the values of \bar{p}_{CO} used here by $1/2.5$ to account for the fact that these

were measured at $\theta_0 = 0.25$ [13], while our values for \bar{p}_{CO_2} are appropriate for $\theta_0 \leq 0.1$. The values for the calculated equilibrium CO₂ reaction probability are shown in figure 2 as a function of temperature (in Arrhenius form), along with the error bars due to the error bars on $(P_{\text{CO}_2}/P_{\text{CO}})_{\text{eq}}$. The slope of the calculated CO₂ reaction probability corresponds to an apparent activation energy of $\sim 18 \pm 1$ kcal mol⁻¹, which just reflects the sum of the ΔH^0 for reaction (6), $\sim 12 \pm 1$ kcal mol⁻¹, and the apparent activation energy for \bar{p}_{CO} (~ 6 kcal mol⁻¹, [13]). This slope compares reasonably well to the experimentally observed apparent activation energy of 16.4 kcal mol⁻¹ for the instantaneous rate at $\theta_0 = 0.1$.

The absolute values of the calculated dissociative adsorption probabilities for CO₂ are in reasonable agreement with the results of our present experiments, which showed $\bar{p}_{\text{CO}_2} \approx 10^{-9}$ – 10^{-11} in this temperature range, falling just inside the lower limit of the error bars for the calculated \bar{p}_{CO_2} . Note that the error bars on the calculated curve include no contribution from possible experimental errors in \bar{p}_{CO} . Indeed, the values for \bar{p}_{CO} which we have used here from [13] are somewhat higher than those of [14]. Using the latter would bring the calculated \bar{p}_{CO_2} into better agreement with our results. It should be pointed out here that the coverage of CO_a under the equilibrium conditions of figure 3 at $\bar{p}_{\text{CO}_2} = 650$ Torr can be shown to be quite small using the known activation energy and kinetics for CO desorption and adsorption on Cu(110) [27]. Thus it is expected that CO_a would not complicate the comparison to our results by inhibiting the dissociative adsorption of CO₂ under such equilibrium conditions.

The equilibrium CO₂/CO pressure ratios we have calculated at $\theta_0 \approx 0.1$ in figure 3 based upon our estimate of ΔG^0_{f} are reasonably consistent with the measured reaction probabilities for the (non-equilibrium) reactions: CO₂ → CO + O_a and CO + O_a → CO₂. However, these ratios are approximately three orders of magnitude larger than those reported for Cu–Al₂O₃ and Cu–ZnO–Al₂O₃ under methanol synthesis conditions by Chinchen *et al* [6], who estimated by indirect means that the oxygen coverage was ~ 0.25 at $P_{\text{CO}_2}/P_{\text{CO}} = 1.0$ and 513 K. They made these measurements under the methanol synthesis conditions, so clean-off reactions by H₂ (H₂ + O_a → H₂O) should make the disagreement with the present calculations even worse. There is clearly a strong inconsistency here which cannot be easily explained. A more direct measurement of the oxygen coverage under the conditions of Chinchen *et al* would be useful. It is possible that certain copper facets on polycrystalline Cu–Al₂O₃ are more active for CO₂ dissociation than is Cu(110), although the (110) plane is expected to be one of the most active facets due to its microscopic roughness. Also, there is not a large structural sensitivity in the reverse reaction [13], which implies by microscopic reversibility that dissociative CO₂ adsorption is also not very structurally sensitive. Other impurity elements present on Cu–Al₂O₃ could also have promoted CO₂ dissociation. In any case, the value for the standard free energy of formation of O_a on copper of -57 kcal mol⁻¹ derived by Chinchen *et al* [6] from their observations of θ_0 versus $P_{\text{CO}_2}/P_{\text{CO}}$ at 513 K disagrees significantly with the value which we estimate (-46 kcal mol⁻¹) based upon the calorimetric heat of adsorption of oxygen on polycrystalline Cu (see equation (5)). The value of Chinchen *et al* would require a ΔS for reaction (3) of *positive* 2 cal mol⁻¹ K⁻¹, compared to *negative* 19 ± 4 cal mol⁻¹ K⁻¹ which we estimate.

Van Herwijnen and deJong [28] have measured rates of the reverse water-gas shift reaction over a Cu–ZnO catalyst at low conversions. Assuming that the reaction occurs only on the metallic Cu surfaces and that $\sim 50\%$ of the BET surface area is Cu, we calculate a specific rate of $\sim 10^{13}$ molecules cm⁻² s based upon their rate data at 528 K and their lowest CO₂ pressure (~ 0.07 atm), where the rate is approaching first order in

CO₂ pressure. This corresponds to a reaction probability of 5×10^{-10} per collision of CO₂ molecules with the Cu surface. This value is reasonably close to the probability ($\sim 2 \times 10^{-10}$) which we have observed (figure 2) for the dissociative adsorption of CO₂ at 530 K on Cu(110), and well within the range estimated from thermodynamic considerations and a knowledge of \bar{p}_{CO} . This comparison, which is quite favourable given the magnitude of potential errors and impurity effects, supports a mechanism for reverse water gas shift whereby the rate-determining step is the dissociative adsorption of CO₂ to produce O_a. The O_a would then be consumed rapidly by the reaction $\text{H}_2 + \text{O}_a \rightarrow \text{H}_2\text{O}$, which is known to occur on Cu surfaces with a relatively higher probability of about 10^{-5} – 10^{-7} per H₂ collision with the surface when significant O_a concentrations are present [13, 26]. (Note that H₂ is thought first to adsorb dissociatively in achieving this overall step [26, 31].) From the kinetic data of [28], we calculated an apparent activation energy of ~ 25 kcal mol⁻¹ for the reverse water-gas shift rate at conditions of low P_{CO_2} . This can be compared to activation energies of 18 and 17 kcal mol⁻¹ calculated and measured here for the dissociative adsorption of CO₂ at $\theta_0 = 0.1$, which suggests that a large part of the barrier to the reverse water-gas shift reaction involves dissociative CO₂ adsorption.

Our results in figure 2 indicate a strongly positive activation energy for CO₂ dissociative adsorption on Cu(110), such that the dissociation probability would be expected to be diminishingly small near or below room temperature ($p_{\text{CO}_2} \leq 3 \times 10^{13}$). This is in contrast to previous experiments on various Cu samples including Cu(110), where CO₂ dissociation was claimed to be facile at or below room temperature [3–5]. We do not understand the reasons for this discrepancy, but it could be due to impurities in CO₂ or on the surface in those studies.

The apparent activation energy for the dissociative adsorption of CO₂ we observe here is undoubtedly related to the energy required to cleave the C–O bond. While some surfaces such as Ni(110) [18] and Fe(110) [19] dissociatively adsorb CO₂ with relatively high probability even in UHV, more passive surfaces such as Pt(111) show no affinity for dissociating CO₂ [29]. In the case of Pt(111) a substantial activation barrier is also expected since CO₂ molecules incident on the surface with a component of translational energy perpendicular to the surface of up to 3.2 kcal mol⁻¹ were unable to produce significant dissociative adsorption [29]. In the case of CO₂–Ni(100), the dissociation barrier becomes accessible as the CO₂ energy is increased from 2 to 25 kcal mol⁻¹ [30].

As can be seen in figure 1(a) at ≤ 530 K, the uptake curves are clearly much less steep above ~ 15 s exposure than below 10 s exposure. This decrease in slope is not so strong in figure 1(b) at only 65 Torr CO₂. This reflects the fact that the dissociation rate shows a reaction order with respect to CO₂ pressure which decreases from unity to ~ 0.7 as θ_0 increases. This decrease in reaction order may be due to the fact that molecularly adsorbed CO₂ is present in concentrations sufficient to significantly poison surface sites only at higher CO₂ pressures and higher θ_0 . An increase in the heat of adsorption of CO₂ due to the presence of O_a could explain such a result. The change in slope in figure 1(b) may also be due to more facile dissociation of CO₂ at surface impurities or defects which are in unobservedly low concentrations, but which saturate after a short time. Surface caesium, for example, leads to a dissociative adsorption probability for CO₂ on Cu(110) of nearly unity [16]. We show here that surface carbonate cannot be produced on clean Cu(110), at least under our conditions. In contrast, Chinchin *et al* [31] have provided evidence for the formation of an O–CO₂ complex on Cu–ZnO catalysts. It should be noted that carbonate is readily produced on Cs-doped Cu(110) [16]. An interesting fundamental question for further investigation is why carbonate is readily

produced via the reaction $\text{CO}_2 + \text{O}_a \rightarrow \text{CO}_{3,a}$ on Ag(110) [20], but is not produced even under much more extensive exposures on oxygen-dosed Cu(110).

5. Conclusions

Our results indicate that there is no measurable adsorption or dissociation of CO₂ on Cu(110) under UHV conditions. At high pressures, dissociation of CO₂ was observed but with a reaction probability lower than $\sim 10^{-9}$ per collision of CO₂ molecule with the surface, and an apparent activation energy of ~ 16 kcal mole⁻¹. These results are supported by equilibrium considerations based on a knowledge of the kinetics of the reverse reaction ($\text{CO}_g + \text{O}_a \rightarrow \text{CO}_{2,g}$) and a thermochemical analysis. They suggest that the reverse water-gas shift mechanism occurs via an O_a intermediate. The results also show that CO₂/CO pressure ratios in excess of ~ 100 are required to establish significant concentrations of O_a in the temperature range of interest for the methanol synthesis reaction (<600 K), at least on pure Cu surfaces.

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