Kinetics of Adsorption, Replacement and Catalysis in the Interaction of O_2 and CO with Clean Nickel Surfaces *

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The kinetics of the interaction of O_2 with CO on Ni films under ultra-high vacuum conditions has been investigated utilizing an apparatus designed for sticking probability profile measurement. With it, absolute rates of adsorption, replacement and catalysis, and surface coverages in the reacting species were simultaneously measured. The results reveal marked differences in the chemical reactivity of the different binding states in the adlayer. The catalytic reaction of preadsorbed O_2 with gaseous CO to form CO_2 was found to proceed only when the coverage θ in the preadsorbed O_2 layer was $< \frac{1}{4}$ monolayer. The catalytically active species β'-O_2 is converted to a more tightly bound, inert species β-O_2 at $\theta_{O_2} > \frac{1}{4}$ monolayer, this transformation having a marked effect on the sticking probability profile for O_2 on Ni.[4] Reaction kinetics indicate that the β'-O_2 state is non-dissociatively adsorbed. When gaseous O_2 is introduced to Ni films with preadsorbed CO, the CO is efficiently and quantitatively displaced from the surface as CO and CO_2. The strongly bound β-CO state yields CO_2 and a more weakly bound α-CO state yields CO, both processes being preceded by a short induction period. Reaction mechanisms are proposed which are supported by infra-red data obtained from supported nickel-on-silica samples. The continuous catalytic reaction of CO with O_2 to form CO_2 over O_2-presaturated Ni films was also examined, and a possible reaction mechanism is discussed.

The reaction between CO and O_2 to form CO_2 catalyzed by clean nickel surfaces [1] was selected for a kinetic investigation owing to our previous experience with clean Ni films.[2-4] The study was performed utilizing an apparatus designed to measure the adsorption efficiencies for the collision of gases with metal films formed under ultra-high-vacuum conditions,[4, 5] an apparatus well-suited to the kinetic study of catalytic reactions. With it, the following parameters may be simultaneously and continuously measured: (i) absolute rates of product formation; (ii) absolute rates of replacement processes; (iii) sticking probabilities of reacting gases; and (iv) overall surface coverages in the reacting species. In addition, the apparatus affords a simple and unequivocal means of distinguishing between Langmuir–Hinshelwood kinetics,[6] in which reaction only takes place between reactants adsorbed on adjacent sites, and Rideal–Eley kinetics,[7] in which reaction takes place between a chemisorbed species and a molecule in a van der Waals layer.

Before undertaking the present study, the separate interactions of O_2 and of CO with Ni films were examined.[3, 4] Surface structural rearrangements during the successive interaction of O_2 and CO with Ni single crystals, determined by LEED, have been reported for the (110),[8] (100),[9, 10] and (111) [11] planes, and surface potential changes during the adsorption of O_2 and CO on Ni films at 90 K have been reported by Siddiqi and Tompkins.[12] The reaction between CO and O_2 over heavily oxidized Ni films has been studied by Roberts and Wells [13] by the surface potential technique.

EXPERIMENTAL

The apparatus has been described elsewhere.[4]   Metal films were deposited under ultra-high-vacuum conditions ($<10^{-9}$ Torr *) on the walls of a spherical glass vessel.   During adsorption, the gas or gas mixture is allowed to flow into the reaction vessel at a measured rate from a centrally placed spherical diffuser so as to obtain a uniform impingement rate at all points on the metal surface.   Sticking probabilities are determined from the rate of gas inflow r_i (molecules s^{-1}) and the partial pressure P (Torr) of the impinging gas as determined by a mass spectrometer, calibrated with a Redhead-modulated ionization gauge, positioned so as to sample only gas-phase molecules reflected from the metal film surface and not molecules coming directly from the diffuser.   The sticking probability s is obtained from the expression

$$s = r_i/[r_i + 3.5 \times 10^{22} \, aP/(MT)^{\frac{1}{2}}], \qquad (1)$$

where a is the geometric area of the metal film (500 cm^2), M is the molecular weight of the impinging gas, and T the temperature of the mass spectrometer side-arm.   In general, r_i (= adsorption rate) was maintained at 10^{14}-10^{15} molecules s^{-1}; thus, 10^{15} molecules cm^{-2} are adsorbed in 10-100 min.

In studying the interaction of two gases, A and B, two procedures may be followed.   (i) Gas A is adsorbed to a determined coverage, adsorption terminated, and gas B introduced at a rate $r_{i,B}$.   The sticking probability is determined from eqn (1); if gas A is displaced by gas B, the rate of displacement (molecules cm^{-2} s^{-1}) is given by

$$-\frac{dN_A}{dt} = \frac{1}{a}\left(FP_A + \frac{V}{kT}\frac{dP_A}{dt}\right), \qquad (2)$$

where P_A is the partial pressure of A in the vessel, F is the conductance (molecules Torr^{-1} s^{-1}) of the diffuser and V is the volume of the reaction vessel; in general the second term in parentheses may be ignored, and the rate of displacement is directly proportional to the partial pressure of the displaced gas.   If reaction occurs between A and B to form a product C, the rate of formation (molecules cm^{-2} s^{-1}) of C is

$$\frac{dN_C}{dt} = \frac{1}{a}\left(FP_C + \frac{V}{kT}\frac{dP_C}{dt}\right). \qquad (3)$$

The total surface coverage at any instant is determined from the known rates of gas inflow and the period over which this has occurred, and the rate at which displacement and reaction products are removed from the cell:

$$dN_{B,C}/dt = FP_{B,C}/a. \qquad (4)$$

(ii) The two gases are allowed to flow into the cell at determined and variable rates, with the valve between the reaction vessel and the pumps in the open position, until steady-state conditions are reached.   The rate of formation of product C is then simply given by

$$dN_C/dt = (F' + F)P_C/a, \qquad (5)$$

where F' is the conduction of the exhaust tubulation.   The pressure dependences of the reaction rate for each of the reactants is obtained by varying the inflow rates, and hence steady-state partial pressures of A and B.

RESULTS AND DISCUSSION

REACTION OF CARBON MONOXIDE WITH PREADSORBED OXYGEN

PRESENTATION AND ANALYSIS OF THE RESULTS

The interaction of CO and O_2 preadsorbed on Ni films at 300 K was markedly sensitive to the extent of oxygen uptake.[3]   With 25×10^{14} O_2 molecules cm^{-2} (geometric area) (corresponding to a monolayer of adsorbed O atoms [4]), and with 20×10^{14}

* 1 Torr = 133.3 Nm^{-2}

O_2 molecules cm^{-2} (80 % of a monolayer) preadsorbed, an appreciable amount of CO was adsorbed ($\sim 3 \times 10^{14}$ molecules cm^{-2}). No O_2 was displaced from the surface, however, and the rate of CO_2 formation was negligibly small ($< 10^7$ molecules $cm^{-2}\, s^{-1}$). However, when O_2 preadsorption was terminated at 4×10^{14} molecules cm^{-2} (< 20 % of a monolayer) the reaction of this adlayer with gaseous CO to form CO_2 proceeded readily.
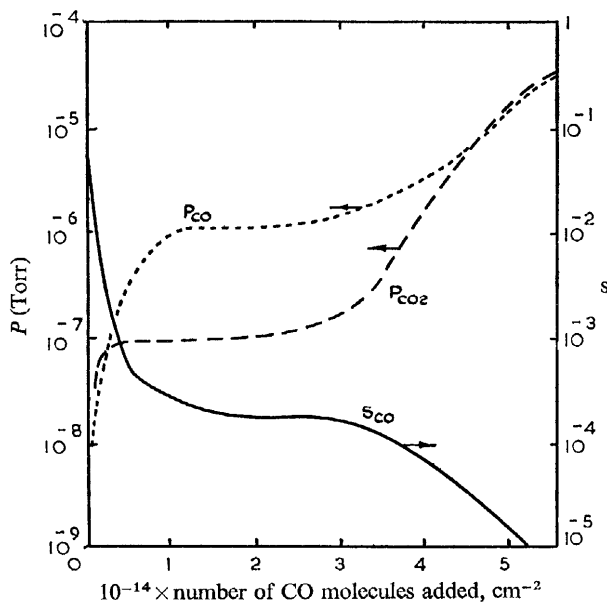

FIG. 1.—The interaction of CO at 300 K with 4×10^{14} molecules cm^{-2} geometric area O_2 preadsorbed on Ni at 300 K.

At coverages above $\frac{1}{4}$ monolayer (5×10^{14} molecules cm^{-2}) the O_2 adlayer undergoes a slow phase change [4] from a state designated β', stable only at low coverages, to a state designated β; at a coverage of 4×10^{14} molecules cm^{-2} the β' state is completely stable. The sticking probability profile for CO adsorption on the β' structure (fig. 1) shows an initial sharp fall from 0.1 to a plateau at 2×10^{-4}, finally falling to 10^{-5} at a total CO uptake of 5×10^{14} molecules cm^{-2}. The relative inactivity of the surface to CO adsorption is unexpected, since some 4/5 of the surface sites should be bare, and CO adsorption on *clean* Ni surfaces proceeds with $s = 1$ up to high coverages.[3] This ability of β'-O_2 to " saturate " the Ni surface at low coverages was also apparent from the sticking probability profile for O_2 on Ni, where s falls monotonically with increasing β' coverage, and only rises as the $\beta' \to \beta$ conversion takes place. Similarly, pre-adsorption of 4×10^{14} O_2 molecules cm^{-2} resulted in a marked reduction in the amount of nitrogen taken up by the Ni film at 77 K, from 22×10^{14} N_2 molecules cm^{-2} for a clean film to 9×10^{14} N_2 molecules cm^{-2} for a β'-covered film (1/5 monolayer).

The catalytic production of CO_2 is in this case appreciable (fig. 1); thus, at a CO pressure of 3×10^{-5} Torr, CO_2 is produced at 4×10^{10} molecules $cm^{-2}\, s^{-1}$. Details of the kinetic mechanism can be deduced from the data of fig. 1 The rate of CO_2 production rapidly rises to a plateau when CO is first allowed to flow into the cell, *remains constant while the CO surface coverage increases*, and finally rises to a substantial level as the CO *pressure* is increased. If Langmuir–Hinshelwood kinetics

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were operative, the CO_2 production rate should increase with increasing coverage in chemisorbed CO, in contrast to the present results; on the other hand, with Rideal–Eley kinetics, the rate of CO_2 production should be related to the CO pressure, as observed here.   Under the conditions of the experiment, when the CO pressure had risen to 2×10^{-5} Torr the total amount of CO_2 produced was small ($\sim 0.2 \times 10^{14}$ molecules cm^{-2}), and the coverage in β'-O_2 may be assumed to be invariant; the reaction order in CO gas-phase pressure may therefore be directly deduced from the slope of a [log (dN_{CO_2}/dt),log P_{CO}] plot, shown in fig. 2.   The plot is linear, within experimental error, with slope 2.0 ± 0.3.

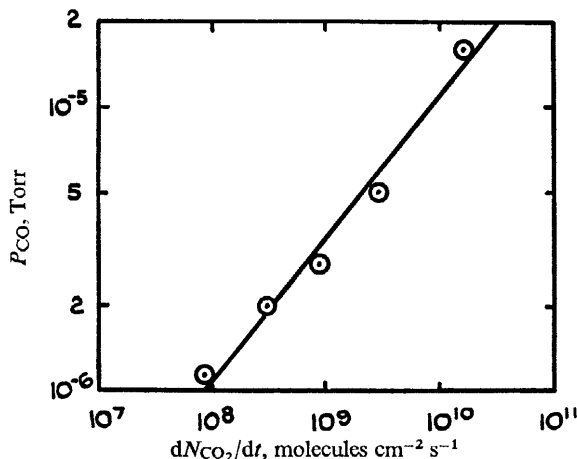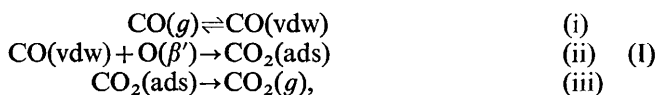FIG. 2.—The increase of CO_2 production rate as a function CO pressure for the interaction of gaseous CO with preadsorbed β'-O_2 at 300 K.
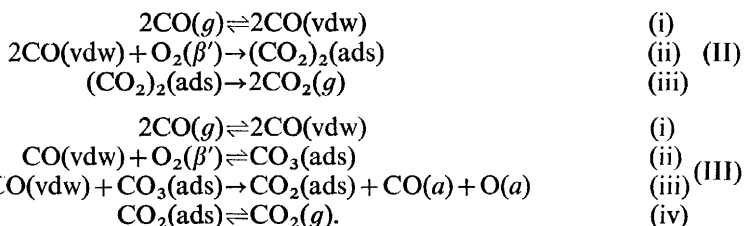
REACTION MECHANISM

The reaction of CO with β'—O_2 to produce CO_2 proceeds through a Rideal–Eley mechanism, and is second-order in the CO pressure.   If the β' state were a dissociatively adsorbed species, the following simple reaction sequence would be expected:

$$CO(g) \rightleftharpoons CO(vdw) \qquad \qquad \text{(i)}$$
$$CO(vdw) + O(\beta') \rightarrow CO_2(ads) \qquad \text{(ii)} \quad \text{(I)}$$
$$CO_2(ads) \rightarrow CO_2(g), \qquad \qquad \text{(iii)}$$

where CO(vdw) is a physisorbed state.   Inserting a Henry-law proportionality between surface coverage in CO(vdw) and the CO pressure, and with steps (ii) or (iii) rate determining, this yields the rate equation

$$dN_{CO_2}/dt = k[O(\beta')]P_{CO}$$

which is not in accord with experiment.   On the other hand, if the β' state is non-dissociatively adsorbed, one of the following reaction sequences would be expected:

$$2CO(g) \rightleftharpoons 2CO(vdw) \qquad \qquad \text{(i)}$$
$$2CO(vdw) + O_2(\beta') \rightarrow (CO_2)_2(ads) \qquad \text{(ii)} \quad \text{(II)}$$
$$(CO_2)_2(ads) \rightarrow 2CO_2(g) \qquad \qquad \text{(iii)}$$

$$2CO(g) \rightleftharpoons 2CO(vdw) \qquad \qquad \qquad \text{(i)}$$
$$CO(vdw) + O_2(\beta') \rightleftharpoons CO_3(ads) \qquad \qquad \text{(ii)}$$
$$CO(vdw) + CO_3(ads) \rightarrow CO_2(ads) + CO(a) + O(a) \qquad \text{(iii)} \quad \text{(III)}$$
$$CO_2(ads) \rightleftharpoons CO_2(g). \qquad \qquad \qquad \text{(iv)}$$

Both sequences lead to the experimentally-observed second-order dependence on the CO pressure, but sequence (II) may be eliminated due to the small probability of the 3-body collision in step (ii). Reaction sequence (III) is similar to that postulated by Heyne and Tompkins [14] for the catalytic production of CO_2 from CO and O_2 over Pt surfaces. Park and Farnsworth [3] and Germer and MacRae [15] have noted that reaction of CO at 300 K with a " (1X2)—O " structure, initially formed by O_2 adsorption on a Ni(110) surface, causes its conversion to a " (1X3)—O " structure. This evidence favours step (iii) in sequence (III), in which an adsorbed O atom is retained on the surface.

We conclude that the catalytically reactive β'-O_2 state, stable on Ni surfaces at $\theta < \frac{1}{4}$, is probably non-dissociatively adsorbed. At $\theta > \frac{1}{4}$, this state is converted to β—O_2, which is catalytically inert towards gaseous CO : it is probable that this strongly bound, inactive species is dissociatively adsorbed. Furthermore, reaction of β'-O_2 does not occur with the chemisorbed CO layer formed when CO is introduced; instead the reaction takes place by a Rideal–Eley mechanism through a weakly held CO state in equilibrium with gas-phase CO, presumably held in a van der Waals second layer over the β'-O_2 chemisorbed state.

REACTION OF OXYGEN WITH PREADSORBED CARBON MONOXIDE

QUALITATIVE DESCRIPTION OF KINETIC RESULTS

In three separate experiments, Ni films were covered with CO until the sticking probability had fallen to 10^{-4} at temperatures of 195, 300 and 373 K. At these temperatures O_2 was then allowed to flow into the cell : results obtained at 300 K are presented in fig. 3.
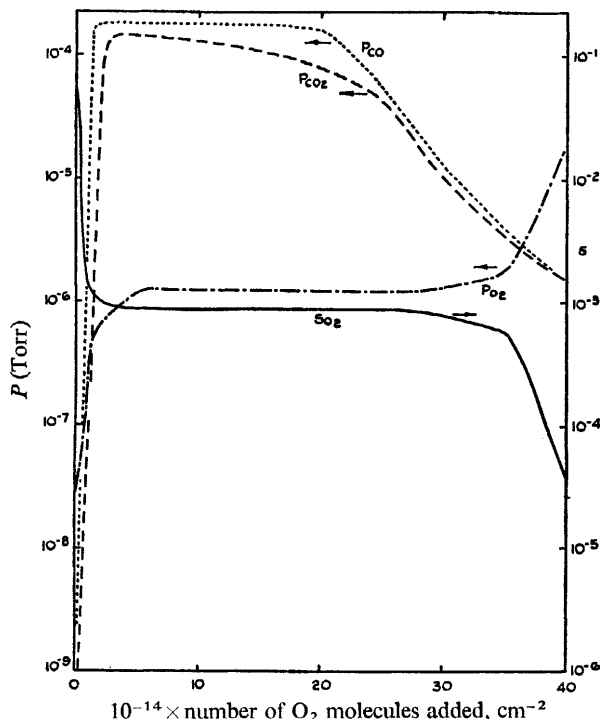

FIG. 3.—The interaction of O_2 with preadsorbed CO at 300 K.

At 300 and 373 K the O_2 uptake is large, approximating closely to the amount taken up by clean Ni films [4] ; the sticking probability profile is, however, quite different from those for clean films, for which the initial s value is unity and a pronounced minimum occurs at 5×10^{14} molecules cm^{-2}.   Both CO and CO_2 are desorbed from the surface as a result of bombardment with O_2, and at 300 and 373 K the entire CO adlayer is finally displaced from the surface by O_2.   At 195 K only about 15 % of the pre-adsorbed CO was removed, and an equivalent, small amount of O_2 was adsorbed : this does not, however, preclude the possibility of further reaction at this temperature with higher O_2 pressures.   The reactivity of preadsorbed CO on Ni films to gaseous O_2 has been established by Siddiqi and Tompkins [12] and Kawasaki et al.,[1] although the simple displacement of CO, with the appearance of CO in the gas phase, was not noted by the latter authors.

QUANTITATIVE ANALYSIS OF KINETIC RESULTS

As O_2 is introduced to the CO-covered Ni surfaces, the rates of CO and CO_2 production rapidly attain a maximum value, and then fall gradually as the O_2 surface coverage is increased : the rates are clearly independent of the total amount of chemsorbed O_2, again indicating that reaction takes place through a Rideal–Eley mechanism.   The interaction with the chemisorbed CO layer to produce $CO(g)$ and $CO_2(g)$ proceeds either through direct collision of gas phase O_2 or through a weakly bound (van der Waals) O_2 adlayer which is rapidly equilibrated with the gas phase.

TABLE 1

wt. of film (mg)	temp. (K)	CO preadsorbed (molecules cm^{-2})	CO desorbed (molecules cm^{-2})	CO_2 desorbed (molecules cm^{-2})	total CO and CO_2 desorbed (molecules cm^{-2})
15.5	195	18×10^{14}	1.7×10^{14}	0.9×10^{14}	2.6×10^{14}
21.2	300	15×10^{14}	9.3×10^{14}	5.6×10^{14}	14.9×10^{14}
14.0	373	8.5×10^{14}	3.4×10^{14}	5.7×10^{14}	9.1×10^{14}

The total amounts of CO and CO_2 desorbed during the reaction up to any instant t, where O_2 is introduced at $t = 0$, may be calculated from the integrated form of eqn (4) :

$$N_{CO,CO_2} = \frac{F}{a} \int_0^t P_{CO,CO_2} dt. \qquad (6)$$

The integration was performed graphically, and results for $t = \infty$ are presented in table 1 : within experimental error, at 300 and 373 K, the amount of CO preadsorbed is equal to the total of CO and CO_2 desorbed showing that the surface is purged of CO by the interaction with O_2.   Furthermore, the amounts of CO_2 produced by the interaction at 300 and 373 K are the same, but the amount of CO produced at 300 K is more than twice that produced at 373 K.   From studies of CO on Ni films,[16,17,4] two states may be identified, a strongly bound state, designated β, which does not desorb at $T < 373$ K, and a less strongly bound state α, with a coverage dependent heat of adsorption : the α-state is only partially occupied at 373 and 300 K at CO pressures of $\sim 10^{-10}$ Torr, while the β-state population at 300 and 373 K is the same. It is therefore deduced that *CO$_2$ formation results from the interaction of O_2 with the β-CO state, while CO displaced into the gas phase originates from α-CO on the surface*.   This conclusion was verified in an experiment in which CO adsorption on a clean Ni surface at 300 K was terminated at 5×10^{14} molecules cm^{-2}, at which stage only the β-CO state is appreciably occupied : on allowing O_2 to flow into the cell, only CO_2 and O_2 were detected in the gas phase (only a small CO$^+$ signal, 12 % of

that for CO_2^+, which gives the expected ratio for the cracking of CO_2 in the mass spectrometer, was observed). Thus the production of CO_2 and of CO occurs through two distinct processes, a factor which greatly simplifies the quantitative analysis of the kinetic data.

The data were analyzed by the following procedure. Rates of CO and CO_2 production are calculated from eqn (3). Fractional coverages θ in α-CO and β-CO at any time t during O_2 interaction are obtained by adapting eqn (6):

$$\theta_{(\alpha\text{-CO})} = \theta_{(\alpha\text{-CO})}^{\circ} - \frac{F}{N_{CO}^{\infty}a}\int_0^t P_{CO}dt, \tag{7}$$

$$\theta_{(\beta\text{-CO})} = \theta_{(\beta\text{-CO})}^{\circ} - \frac{F}{N_{CO_2}^{\infty}a}\int_0^t P_{CO_2}dt, \tag{8}$$

where θ° is the fractional CO coverage at $t = 0$, and N_{CO}^{∞} and $N_{CO_2}^{\infty}$ are the total amounts of CO and CO_2, in molecules cm^{-2}, produced at $t = \infty$ (see table 1). The α-CO state is incompletely filled at temperatures > 195 K, whence the coverage $\theta_{\alpha\text{-CO}}^{\circ}$ was normalized to $\theta_{\alpha\text{-CO}}^{\circ} = 1$ at 195 K. The saturation coverage in the α state, $N_{\alpha\text{-CO}}^s$, was thus taken as the experimental value at 195 K, viz., 12.3×10^{14} molecules cm^{-2}. From table 1, it follows that $\theta_{\alpha\text{-CO}}^{\circ} = 0.75$ at 300 K, and $\theta_{\alpha\text{-CO}}^{\circ} = 0.25$ at 373 K.

TABLE 2.—KINETIC ANALYSIS OF THE DISPLACEMENT OF ADSORBED α-CO BY GASEOUS O_2; RATE CONSTANTS k_{CO} REFER TO $m = \frac{1}{2}$ AND $n = 1$ IN EQN (9)

temp. (K)	$N_{CO} \times 10^{-14}$ desorbed (molecules cm^{-2})	$\theta_{(\alpha\text{-CO})}$	P_{O_2} (Torr)	$P_{O_2}^{\frac{1}{2}}$ (Torr)$^{\frac{1}{2}}$	$\frac{dN_{CO}}{dt}$ (molecules $cm^{-2} s^{-1}$)	k_{CO} (molecules cm^{-2} s^{-1} Torr$^{-\frac{1}{2}}$)
195	0.8	0.94	1.6×10^{-6}	1.3×10^{-3}	1.3×10^{10}	1.1×10^{13}
	1.1	0.92	4×10^{-6}	2×10^{-3}	2.7×10^{10}	1.5×10^{13}
	1.5	0.87	7.3×10^{-6}	2.7×10^{-3}	3.1×10^{10}	2.2×10^{13}
300	0.8	0.67	6.4×10^{-7}	8×10^{-4}	1.6×10^{11}	3.0×10^{14}
	2.7	0.51	10^{-6}	10^{-3}	1.6×10^{11}	3.1×10^{14}
	4.6	0.36	10^{-6}	10^{-3}	1.6×10^{11}	4.4×10^{14}
	6.6	0.20	10^{-6}	10^{-3}	1.0×10^{11}	4.0×10^{14}
	7.8	0.1	10^{-6}	10^{-3}	4.3×10^{10}	4.3×10^{14}
373	0.9	0.2	5.6×10^{-9}	7.5×10^{-5}	5.5×10^{10}	3.7×10^{15}
	1.3	0.17	7.7×10^{-9}	8.8×10^{-5}	5.5×10^{10}	3.3×10^{15}
	1.9	0.12	1.3×10^{-8}	1.1×10^{-5}	4.5×10^{10}	3.4×10^{15}
	2.3	0.09	2×10^{-8}	1.4×10^{-4}	4.5×10^{10}	3.6×10^{15}

Since reaction occurs between chemisorbed CO and O_2 in a weakly held, van der Waals layer, the rate equations are of the form

$$dN_{CO}/dt = k_{CO}P_{O_2}^m\theta_{\alpha\text{-CO}}^n, \tag{9}$$

and

$$dN_{CO_2}/dt = k_{CO_2}P_{O_2}^{m'}\theta_{\beta\text{-CO}}^{n'}. \tag{10}$$

The results of the analysis of data in fig. 3, are presented in tables 2 and 3. Self-consistent rate constants, independent of fractional CO coverages ranging between 0.2 and 0.9, and O_2 pressures between 5×10^{-9} and 5×10^{-5} Torr, are obtained with $m = m' = \frac{1}{2}$ and $n = n' = 1$: other combinations of these exponents were tried but did not yield self-consistent rate constants. Arrhenius plots were constructed from

these rate constants and apparent activation energies determined for the two processes. In this way the following empirical rate equations were derived:

$$dN_{CO}/dt = 6.5 \times 10^{17} P_{O_2}^{\frac{1}{2}} \theta_{\alpha\text{-CO}} \exp(-26,000/RT) \qquad (11)$$

and

$$dN_{CO_2}/dt = 5.0 \times 10^{18} P_{O_2}^{\frac{1}{2}} \theta_{\beta\text{-CO}} \exp(-17,000/RT) \qquad (12)$$

where activation energies are expressed in J/mol, and pressures in Torr.

TABLE 3.—KINETIC ANALYSIS OF THE CATALYTIC PRODUCTION OF CO_2 FROM β-CO AND GASEOUS O_2; RATE CONSTANTS k_{CO_2} REFER TO $m' = \frac{1}{2}$ AND $n' = 1$ IN EQN (10)

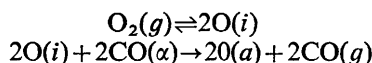| temp. (K)	$N_{CO_2} \times 10^{-14}$ desorbed (molecules cm^{-2})	$\theta_{(\beta\text{-CO})}$	p_{O_2} (Torr)	$P_{O_2}^{\frac{1}{2}}$ (Torr)$^{\frac{1}{2}}$	dN_{CO_2}/dt (molecules cm^{-2} s^{-1})	k_{CO_2} (molecules cm^{-2} s^{-1} Torr$^{-\frac{1}{2}}$)
195	0.3	0.95	9.5×10^{-7}	9.7×10^{-4}	9.0×10^{8}	9.7×10^{11}
	0.4	0.93	2.2×10^{-6}	1.5×10^{-3}	2.3×10^{9}	1.6×10^{12}
	0.6	0.90	5.6×10^{-6}	2.4×10^{-3}	5.0×10^{9}	2.3×10^{12}
	0.9	0.84	4.4×10^{-5}	6.6×10^{-3}	6.7×10^{9}	1.2×10^{12}
300	0.75	0.87	10^{-6}	10^{-3}	1.3×10^{11}	1.5×10^{14}
	1.4	0.76	10^{-6}	10^{-3}	1.3×10^{11}	1.7×10^{14}
	2.0	0.65	10^{-6}	10^{-3}	1.2×10^{11}	1.8×10^{14}
	2.6	0.56	10^{-6}	10^{-3}	1.1×10^{11}	2.0×10^{14}
	3.2	0.45	10^{-6}	10^{-3}	9.8×10^{10}	2.1×10^{14}
	4.1	0.31	10^{-6}	10^{-3}	7.2×10^{10}	2.3×10^{14}
	4.7	0.18	10^{-6}	10^{-3}	4×10^{10}	2.2×10^{14}
373	0.71	0.87	5.0×10^{-9}	7.1×10^{-5}	2.1×10^{11}	3.3×10^{15}
	1.5	0.73	8.0×10^{-9}	9.0×10^{-5}	1.6×10^{11}	2.5×10^{15}
	2.2	0.6	1.0×10^{-8}	10^{-4}	1.4×10^{11}	2.4×10^{15}
	3.0	0.46	1.3×10^{-8}	1.1×10^{-4}	1.5×10^{11}	2.9×10^{15}
	3.8	0.32	1.6×10^{-8}	1.3×10^{-4}	1.4×10^{11}	3.5×10^{15}
	4.6	0.18	1.9×10^{-8}	1.4×10^{-4}	1.0×10^{11}	2.7×10^{15}

REACTION MECHANISM

Before proceeding to discuss possible reaction mechanisms it is useful to summarize relevant experimental factors. (a) When O_2 is introduced to a CO-covered Ni surface there is a short induction period before the rates of CO and CO_2 production rise to a maximum; this period corresponds to the adsorption of $\sim 2 \times 10^{14}$ O_2 molecules cm^{-2}, which is small compared with the total amount of CO preadsorbed. The induction period for the replacement of CO is shorter than that for the production of CO_2 at all temperatures between 195 and 373 K.

(b) After the induction period the CO and CO_2 levels fall monotonically as the CO adlayer is purged from the surface; initially, the rate of O_2 inflow into the cell (= rate of adsorption + rate of O_2 removed as CO_2) is equal to the sum of the rates of CO and CO_2 production, but as the adsorbed CO is progressively removed and the CO and CO_2 production rate falls the rate of O_2 adsorption does not fall.
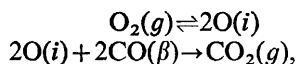
(c) The rates of CO and CO_2 production after the induction period are proportional to the α-CO and β-CO surface coverages, respectively, independent of the *total* oxygen surface coverage, and proportional to the square root of the oxygen pressure. Rideal–Eley mechanisms are thus indicated; however, the square-root dependences

on the oxygen pressure indicate that the rate limiting step in both processes involves a *dissociated* O_2 molecule.
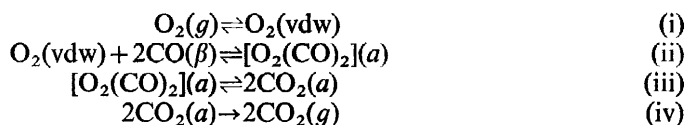
The reactions may be described by the simple overall mechanisms:

$$O_2(g) \rightleftharpoons 2O(i)$$
$$2O(i) + 2CO(\alpha) \rightarrow 2O(a) + 2CO(g)$$

and

$$O_2(g) \rightleftharpoons 2O(i)$$
$$2O(i) + 2CO(\beta) \rightarrow CO_2(g),$$

where $O(i)$ is the intermediate adatom. In both cases, insertion of the Langmuir isotherm in the low coverage limit for dissociative adsorption in the first step generates the experimentally observed dependencies on O_2 pressure and CO coverage. The weakly bound *atomic* oxygen intermediate in equilibrium with the gas phase, although thermodynamically feasible, is unlikely to exist as an independent entity; thus, we consider that an intermediate step occurs in which a surface complex is formed between adsorbed CO and an O_2 *molecule* in the van der Waals layer; thus, for the formation of CO_2 we have

$$O_2(g) \rightleftharpoons O_2(vdw) \tag{i}$$
$$O_2(vdw) + 2CO(\beta) \rightleftharpoons [O_2(CO)_2](a) \tag{ii}$$
$$[O_2(CO)_2](a) \rightleftharpoons 2CO_2(a) \tag{iii}$$
$$2CO_2(a) \rightarrow 2CO_2(g) \tag{iv}$$

where the desorption of CO_2 is rate determining. For the production of CO, step (iv) is simply modified so that an adsorbed O atom and gaseous CO are produced. We envisage the structures in step (iii) to be of the form
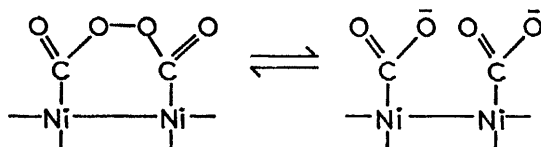
for CO_2 production and
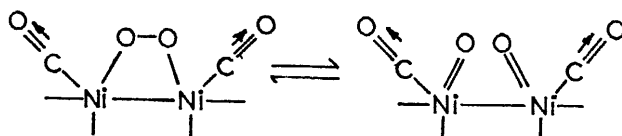
for CO production. It is necessary to postulate the latter alternative structures for CO displacement as the decomposition of an adsorbed CO_2 entity to gaseous CO is not thermodynamically feasible.

The induction period is now ascribed to the absence of steady-state conditions when O_2 is first introduced; during this period the coverages in the intermediates postulated for step (iii) build up to the steady-state values determined by the equilibrium constants for steps (i) to (iii). We note that in step (iv) an adsorption site is vacated at the surface which can be filled by strongly bound, unreactive oxygen from the gas phase. Hence, the mechanism predicts that initially the rate of O_2 inflow will be equal to the sum of the rates of CO and CO_2 production, but as the reaction proceeds and sites are vacated by CO_2 the O_2 adsorption rate will exceed the rates of CO and CO_2 formation; this is also in accord with the results.

In the work described above, the O_2 gas-phase pressure was low —$< 10^{-5}$ Torr— and from the short induction period it can be concluded that the steady-state coverages

in the postulated complexes are low.   On the basis of the mechanism above, increasing the O_2 pressure should displace the steady-state condition towards higher coverages in the complexes, and, since step (iv) is rate determining, lowering the temperature should stabilize the complex on the surface.   Evidence for complex formation on addition of O_2 to a CO-covered Ni film at 90 K was obtained by Siddiqi and Tompkins.[12]   The minimum surface potential obtained on dosing a clean Ni surface with CO was -1.31 V ; on adding O_2 an amount equivalent to about 12 % of the number of CO molecules on the surface was taken up, and the surface potential *increased* to -1.2 V.   On the basis of simple additivity of surface potentials a decrease in surface potential would have been expected, and it was concluded that complex formation occurred.   In principle, it should be possible to observe the vibrations of these complexes using infra-red spectroscopy.

INFRA-RED SPECTRA

For comparison with the kinetic results, it would be desirable to obtain infra-red spectra on Ni films prepared under the same conditions as in the kinetic study, but owing to the experimental difficulties associated with obtaining infra-red spectra for adlayers on low surface area samples, experiments were performed on dispersed Ni-on-SiO$_2$ pressed discs, reduced in hydrogen and subsequently evacuated at 650 K.   The apparatus and procedure have been described by Ravi, King and Sheppard.[18]

With a nickel-on-silica sample cooled to 140 K, admission of CO to a pressure of 10 Torr produced strong bands at 1940 and 2050 cm^{-1} (fig. 7, dashed lines).   This is in close agreement with the results of Eischens *et al.*[19] for CO adsorption on Ni at 300 K, who observed bands at 1905 and 2030 cm^{-1}.   The former was assigned to a bridged carbonyl structure $\begin{smallmatrix} Ni \\ \\ Ni \end{smallmatrix}\!\!>\!C\!\!=\!\!O$, and the latter to a linear N—CiO species.
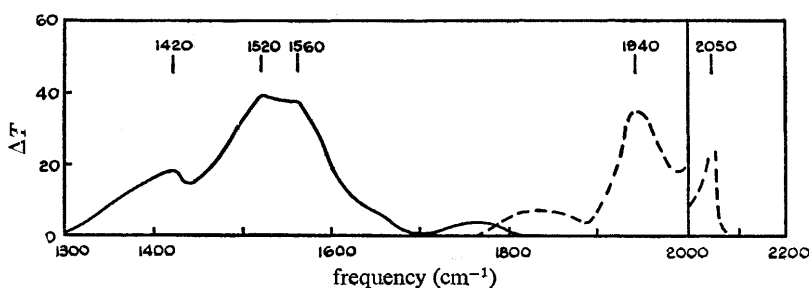

FIG. 4.—Infra-red spectra for adsorbed species on a silica-supported-nickel disc at 140 K : dashed curve, after introduction of CO ; full curve, after the subsequent addition of O_2.   In both cases the background spectrum due to the silica disc has been subtracted from the total transmission obtained with the adsorbed species present to give the transmission difference ΔT.

Subsequent admission of 10 Torr of O_2 with the disc still at 140 K produced a marked change in the infra-red spectrum.   The bands due to adsorbed CO disappeared completely, and three new strong absorption bands appeared at 1420, 1520 and 1560 cm^{-1} (fig. 4, full line).   Clearly, complex formation is induced at the surface by the addition of O_2, in agreement with the kinetic model proposed above.   (At high O_2 pressures the equilibrium represented by step (ii) would be shifted well to the right.) Assignment of the bands to particular structures is difficult ; however, Eischens and Pliskin[20] observed bands at 1560 and 1410 cm^{-1} on adsorption of CO_2 on Ni at

300 K, and Blyholder [21] observed bands at 1560 and 1330 cm⁻¹ following adsorption of CO and O_2 on Ni at 300 K. In the present work, warming to 300 K resulted in almost complete removal of the band at 1420 cm⁻¹, while the bands at 1520 and 1560 cm⁻¹ were reduced in intensity. The results are thus compatible with the presence of two adsorbed complexes, in full accord with the kinetic analysis.

REACTION OF CO WITH O_2 OVER O_2-SATURATED Ni FILMS

PRESENTATION AND ANALYSIS OF RESULTS

With the reaction cell open to the pumps, a mixture of O_2 and CO was allowed to flow over a Ni film, previously saturated with O_2 at 300 K, for 12 h at partial pressures of 5×10^{-5} Torr for both O_2 and CO. After this time interval steady-state conditions, with the O_2, CO and CO_2 pressures time-independent, were achieved. The rate of production of CO_2 may be calculated from the CO_2 partial pressures using eqn (5). The reaction orders in the CO and O_2 pressures and the activation energy for the reaction were determined in three separate experiments.

The exponent x in the CO partial pressure was determined by measuring the variation in the steady-state CO_2 partial pressure as a function of P_{CO} at constant P_{O_2} and temperature (300 K). The results, repeated at three O_2 pressures in the range 10^{-6}-10^{-7} Torr, are plotted as $\log (dN_{CO_2}/dt)$ against $\log P_{CO}$ in fig. 5. The plots show good linearity, with $x = 0.34 \pm 0.02$ (mean value for two different Ni films). To determine the reaction order y in the O_2 partial pressure, the CO partial pressure was maintained constant and P_{O_2} varied over 2 orders of magnitude; the log log plots obtained from four runs are shown in fig. 6, and again linearity is good; the mean value of y from the slopes is 0.50 ± 0.04.
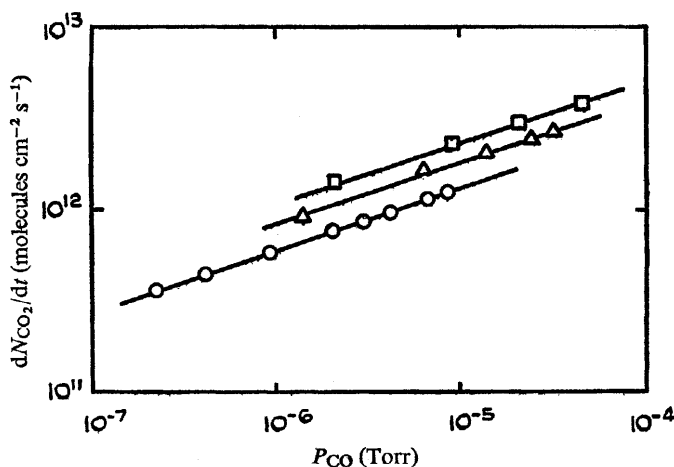

FIG. 5.—The dependence of CO_2 production rate at steady state on CO pressure at constant O_2 pressure: —□—, film I, $P_{O_2} = 9.0 \times 10^{-7}$ Torr; —△—, film I, $P_{O_2} = 4.5 \times 10^{-7}$ Torr; —O—, film II, $P_{O_2} = 10^{-7}$ Torr. Adsorbent temperature, 300 K.

The CO_2 partial pressure in the cell was measured as a function of temperature with P_{O_2} and P_{CO} maintained constant. Arrhenius plots constructed from experiments on two different O_2-saturated Ni films yielded an apparent activation energy of 3.8 ± 1.0 kJ/mol.

Hence, the catalytic production of CO_2 is empirically described by the equation

$$dN_{CO_2}/dt = 5.10^{17}P_{CO}^{\frac{1}{3}}P_{O_2}^{\frac{1}{2}}\exp(-3,800/RT), \qquad (16)$$

where the rate constant is an average value for three O_2-saturated Ni films. The linearity of the plots in fig. 5 and 6 rule out the possibility that the reaction is inhibited by CO_2 adsorption.
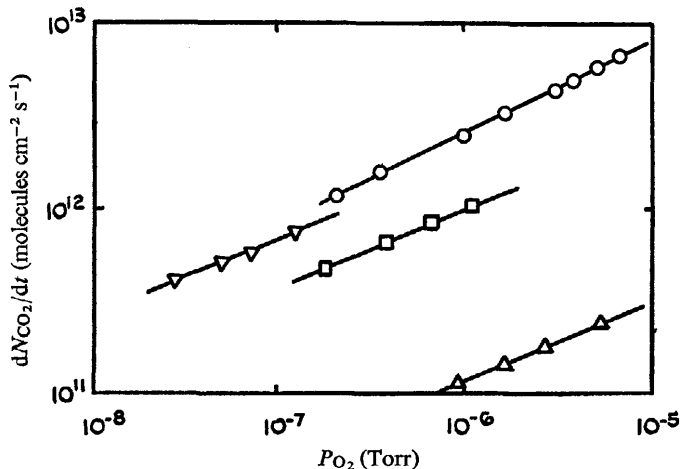

FIG. 6.—The dependence of CO_2 production rate on O_2 pressure at constant CO pressure: —△—, film I, $P_{CO} = 8.0 \times 10^{-7}$ Torr; —□—, film I, $P_{CO} = 3.0 \times 10^{-6}$ Torr; —▽—, film II, $P_{CO} = 1.6 \times 10^{-6}$ Torr; —○—, film III, $P_{CO} = 1.6 \times 10^{-6}$ Torr. Adsorbent temperature, 300 K.

REACTION MECHANISM

Adsorbed O_2 present on Ni at high coverages does not react with gaseous CO; however, chemisorbed CO in the β state reacts readily with gaseous oxygen, and the square-root dependence on the oxygen pressure for the continuous production of CO_2 under consideration here suggests that a similar reaction mechanism is operative. The simple displacement of α-CO from the surface by O_2 is likely to occur during the continuous interaction of O_2 and CO with Ni; however, since the process is independent of that for the production of CO_2, this can be ignored in considering a mechanism for the continuous catalytic production of CO_2.

The reaction order of $\frac{1}{3}$ in the CO pressure suggests that the amount adsorbed in the CO adlayer is related to the CO pressure through a Freundlich isotherm, $\theta = CP^{1/n}$, where $n = 3$. Thus, it is possible to propose a Rideal–Eley mechanism for the continuous production of CO_2 which is in accord with eqn (16), in which O_2 in a van der Waals layer reacts with chemisorbed CO, and the desorption of CO_2 is rate determining. However, unlike the results presented above relating to the *successive* interaction of O_2 and CO, surface coverages in the reacting species have not been monitored during the continuous interaction of O_2 and CO, and conclusions regarding the mechanism must therefore remain speculative.

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