Multipulse Potentiodynamic Studies of the Adsorption of Carbon Monoxide and

Hydrogen on Rhodium Electrodes.   II.   Mixed Adsorption of

Carbon Monoxide and Hydrogen

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At constant potential, a rhodium electrode was allowed to adsorb CO at a constant rate from a dilute solution of the gas in sulfuric acid.   Equilibrium coverages with hydrogen atoms were determined during the course of the CO adsorption process, yielding the hydrogen adsorption isotherms and saturation hydrogen coverages as a function of CO coverage. From the measurements of hydrogen saturation coverage, it is concluded that one CO molecule obscures one hydrogen adsorption site, suggesting one-site attachment of CO to the surface.   Where saturation coverage with hydrogen is not achieved (potentials of 0 v or greater), and for CO coverages less than approximately 75% of maximum, the equilibrium hydrogen coverage decreases linearly with increase in CO coverage.   The same percentage decrease is observed at all potentials above 0 v.   Hence, the shape of the hydrogen adsorption isotherm remains constant with increasing CO coverage.   This in turn implies that CO is not preferentially adsorbed (under conditions of diffusion control) on sites having the highest heats of hydrogen adsorption.

Introduction

In the previous paper,[2a] it was shown that CO adsorption on rhodium may be studied in a quantitative manner (by anodic stripping) if a "multipulse potentiodynamic" sequence is used to establish reproducible initial conditions.   In the present paper, comparisons will be made between the amount of CO and of hydrogen atoms coadsorbed under dynamic conditions.

Experimental Section

Chemicals and equipment were described in the previous paper.[2a]   The rhodium test electrode was similar to the one used previously.   It had a geometric area of 0.08 cm², and the charge, sQ_H, corresponding to "saturation coverage" with hydrogen atoms had the value 0.23 mcoulomb/cm².   The "roughness factor" for the electrode was 1.06 if sQ_H = 0.22 mcoulomb/cm² is taken to correspond to R.F. = 1.0.   As previously,[2a] all values of current and of charge will be reported on the basis of the *geometric* area.   All measurements were made at 80° in a 4 N H_2SO_4 electrolyte.

Procedures and Results

I.   Determination of CO Coverage through Anodic Stripping.   In a solution saturated with CO, the adsorption occurs within 1 sec.[2a]   Under those conditions, the adsorption is diffusion controlled until approximately 80% complete and exhibits a linear dependence on the square root of time.   A linear dependence on the first power of time may be obtained by using a more dilute solution of CO and by agitating the solution, as in the experiments of Figure 1.   The results of Figure 1 show the desired dependence of surface coverage (proportional to Q_{CO}) upon adsorption time for potentials less than 0.5 v and for fractional coverages less than approximately 0.8.   The slow adsorption reaches completion at approximately 100 sec and
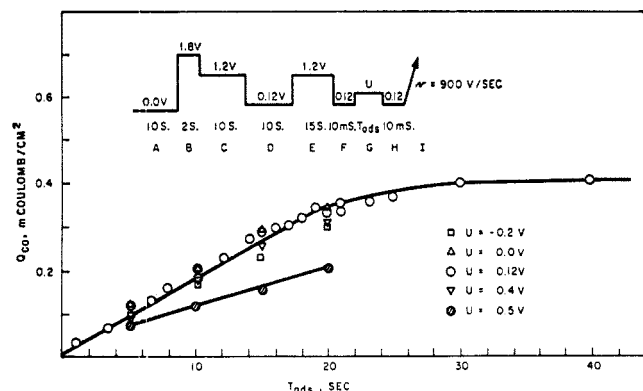
Figure 1. Adsorption of CO on Rh from a stirred solution. The adsorption occurred during step G of the potential sequence. Values of Q_{CO} were determined by application of sweep I. Relative and absolute coverages are directly proportional to Q_{CO}. The 4 N H$_2$SO$_4$ solution was saturated with a gas mixture of 1% CO, 99% argon at 80°. The paddle-stirrer was rotated at 360 rpm.

at a value of Q_{CO} of 0.47 mcoulomb/cm^2 (based on geometric area).

II. Determination of "Saturation Coverage" with Hydrogen Atoms. The sequence of Figure 2 was used in determining the charge, sQ_H, corresponding to saturation coverage of the surface with hydrogen atoms. As previously discussed,[2a] steps A–E of the potential sequence serve to cleanse the surface and to protect it against adsorption of or reaction with a dissolved adsorbate. During step F, the protective "oxygen" film is reduced, and dissolved materials may adsorb. Step G quickly eliminates adsorbed hydrogen. In step H, hydrogen atoms are deposited on the surface, and the corresponding cathodic current is recorded. Trace 1 of Figure 2 was obtained in argon-saturated electrolyte. The current which flows up to point b corresponds mainly to deposition of atomic hydrogen, but also contains contributions to charging of the ionic double layer and to evolution of molecular hydrogen gas. Past point b, the current becomes steeply cathodic corresponding to a sharply increasing rate of H$_2$ evolution. For Rh, the rates of hydrogen atom deposition and H$_2$ evolution are sufficiently sluggish so that the potentials of the cathodic trace have no simple thermodynamic significance at this sweep speed.

Let us make the assumption that the hydrogen atom monolayer is approximately complete before gas evolution becomes very rapid. Then we may attempt to derive the corresponding charge by means of the construction lines on trace 1 of Figure 2. The vertical line c–e was drawn from the point of intersection of tangents b–c and d–c. The line a–e was drawn as an extrapolation of the capacitive current measured above
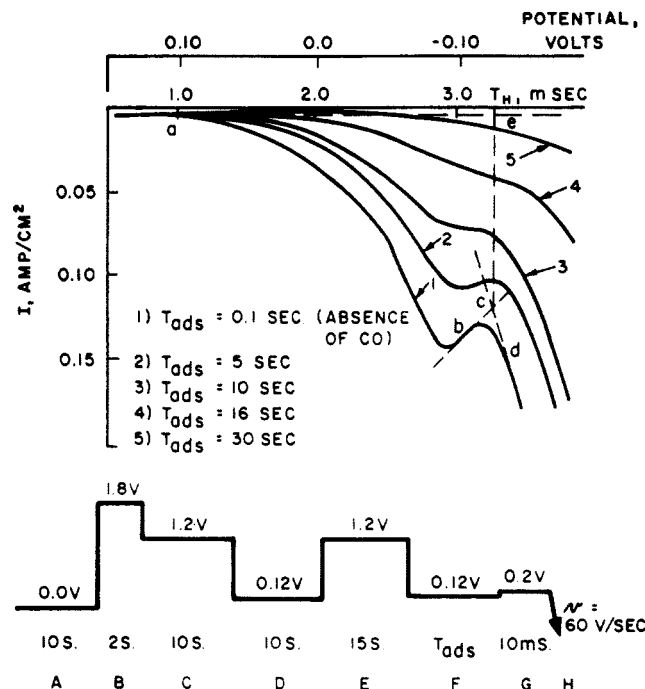

Figure 2. Determination of saturation coverage with hydrogen atoms on a surface partially covered with CO. The adsorption of CO occurred during step F, from 4 N H$_2$SO$_4$ saturated with a gas mixture of 1% CO–99% argon (except 100% argon for trace 1). Traces of hydrogen were removed during step G, and hydrogen was redeposited to saturation during sweep H. The construction lines of trace 1 serve to define a closed area corresponding to the hydrogen charge.

0.1 v. The area aecba is taken as sQ_H. Keeping v constant at 60 v/sec, sQ_H was measured for values of T_{ads} from 0.01 to 100 sec in the argon-saturated solution. This charge was found to maintain the average value of 0.23 mcoulomb/cm^2 with an average deviation of 3%. At much longer values of T_{ads} or when the solution was agitated, sQ_H, was found to decrease. This corresponded to the adsorption of impurities, as already detected[2a] through anodic stripping. Keeping T_{ads} constant at 1 sec and varying v from 10 to 1000 v/sec, sQ_H was again found to remain constant with an average deviation of 5%.

The effect of CO adsorption upon sQ_H was examined in traces 2–5 of Figure 2. As in previous[3] studies, it was ascertained that the cathodic sweep caused no desorption of adsorbed CO. For the CO-containing solution, values of sQ_H are plotted against the adsorption time in Figure 3.

III. Determination of Hydrogen Atom Coverage by Anodic Stripping. At any potential, the charge cor-

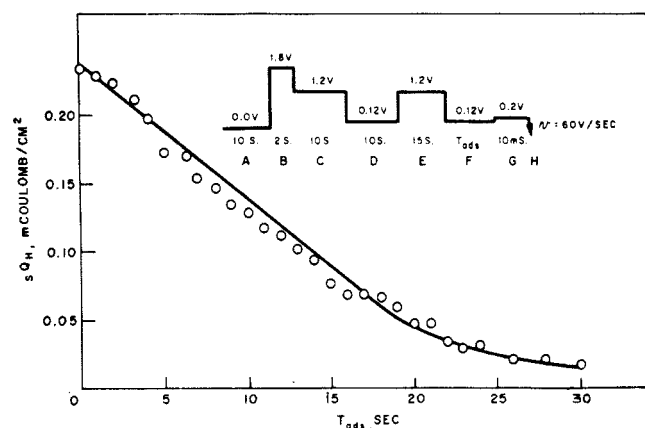(3) S. Gilman, *J. Phys. Chem.*, **67**, 78 (1963).

Figure 3. Variation of saturation coverage with hydrogen as CO is adsorbed on Rh. The saturation coverage with hydrogen is proportional to the charge sQ_H and was determined from traces such as those of Figure 2. The accumulation of CO is given by Figure 1. The 4 N H$_2$SO$_4$ solution was saturated with a gas mixture of 1% CO–99% argon at 80° and was paddle-stirred (360 rpm) throughout the experiment.
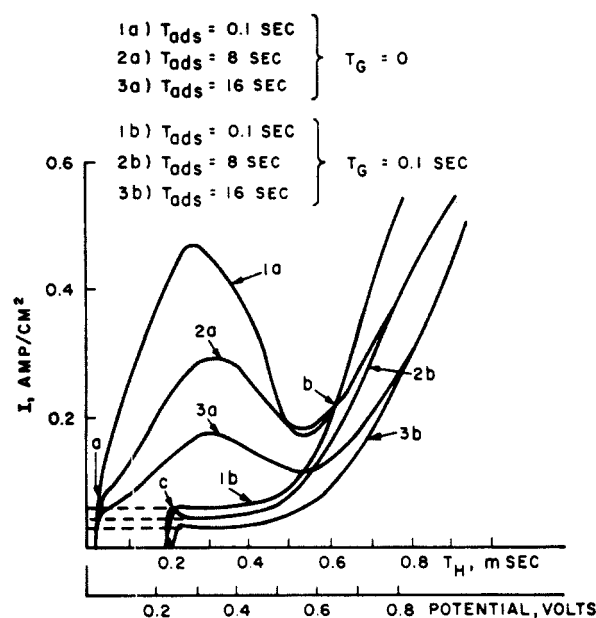

Figure 4. Determination of the hydrogen atom coverage at potential U, during the adsorption of CO. The adsorption occurred during step F from 4 N H$_2$SO$_4$ saturated with a gas mixture of 1% CO–99% argon which was paddle-stirred (360 rpm) throughout the experiment. Traces a were measured during step H without application of step G, and include a current corresponding to stripping of adsorbed hydrogen. Traces b were obtained during sweep H, after previously removing hydrogen during step G. Traces b serve as a correction for currents other than those corresponding to stripping of hydrogen.
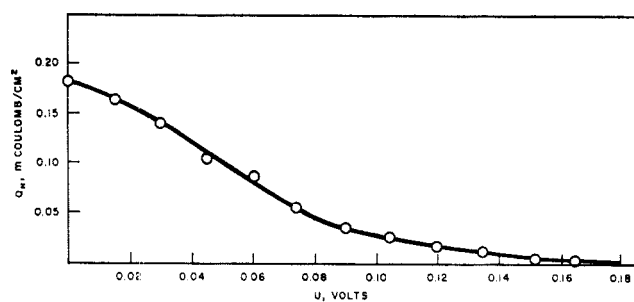
responding to transient hydrogen coverage may be determined by application of a linear anodic sweep. In the sequence of Figure 4, steps A–E serve as electrode pretreatment. The surface is quickly reduced at potential U (step F) and hydrogen atoms are quickly adsorbed on the clean surface. There is subsequent slow desorption of hydrogen as CO adsorbs from solution. The amount of hydrogen present at any moment may be determined by applying sweep H and recording the resulting current–time transient. Trace 1a was obtained for T_{ads} = 0.1 sec and corresponds to the essentially clean surface. The initial current maximum corresponds mainly to the stripping of adsorbed hydrogen. After the minimum, the current rises again as both the surface and adsorbed CO are oxidized. To correct for the nonhydrogen currents, trace 1b was measured after applying step G which quickly eliminates adsorbed hydrogen. Trace 1b was back-extrapolated (c–a) to correct for capacitive charging and the resulting closed area abca defines Q_H. Traces 2 and 3 show how Q_H may also be determined when the surface is largely covered with CO. Values of Q_H were obtained both in the CO-free (Figure 5) and CO-containing solution (Figure 6).

Discussion

I. Structure of the CO Adlayer. From Figure 1, we may obtain the absolute coverage, Γ_{CO}, under transient conditions

$$Q_{CO} = 2F\Gamma_{CO} \qquad (1)$$

Figure 5. Hydrogen coverage on a clean Rh electrode. The hydrogen coverage is proportional to the charge Q_H, measured in the argon-saturated electrolyte by the method of Figure 4.
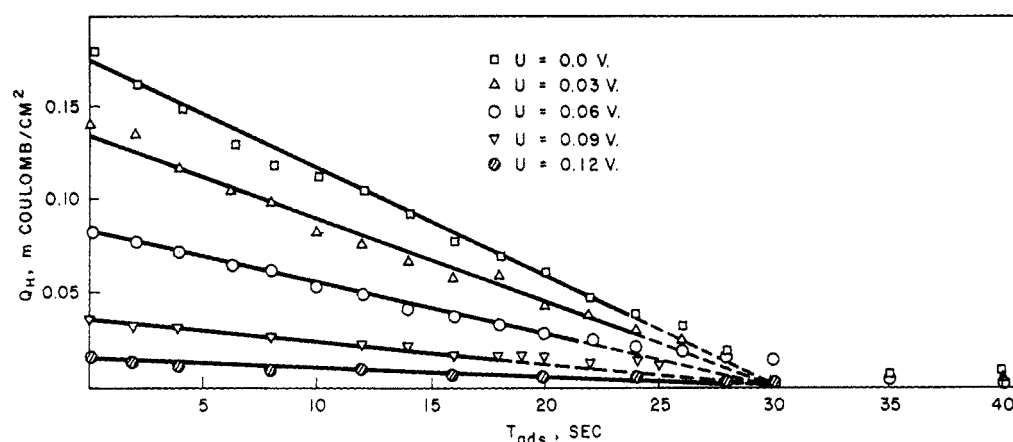
Figure 6. Hydrogen coverage on an Rh electrode partially covered with CO. The charge Q_H was measured by means of the procedures of Figure 4 while CO was adsorbing from 4 N H_2SO_4 saturated with a gas mixture of 1% CO–99% argon (80°), paddle-stirred at 360 rpm. The accumulation of CO under the same circumstances is given by Figure 1.

We see that the rate of adsorption (which is mass transport controlled up to large coverages) is independent of potential over the entire range of adsorption (below 0.5 v). Decreased rates of adsorption above 0.5 v are probably due entirely to the competitive oxidation of CO to CO_2. Under the same conditions, Figure 3 reveals how $_sQ_H$ varies with CO adsorption. For $_sQ_H$, the following relationship may hold

$$_sQ_H = F_s\Gamma_H = F[(_s\Gamma_H)_0 - m\Gamma_{CO}] \qquad (2)$$

where $_s\Gamma_H$ is the "saturation coverage" (moles/cm²) of the surface with H atoms in the presence of some adsorbed CO, $(_s\Gamma_H)_0$ is the "saturation coverage" of the surface with H atoms in the absence of adsorbed CO, and m is the number of hydrogen sites obscured per molecule of CO adsorbed.

Dividing the slope of the plots of Figures 3 and 1 gives us the value of m at any instantaneous value of the coverage with CO. With some scatter, m was found to have a constant value of 0.9 until the coverage is almost complete. This implies that one adsorbed CO molecule occupies one hydrogen adsorption site. This situation contrasts with that found for Pt at lower temperatures.[3] In the latter case, the results suggested that each adsorbed CO molecule occupies two hydrogen adsorption sites ("bridged" structure) in the earlier stage of adsorption, and only one site ("linear" structure) in the later stage of adsorption. These analyses assume, of course, that CO and hydrogen adsorption sites are similar and that hydrogen adsorption is blocked in only a direct manner by the formation of the surface–organic bond.

II. The Hydrogen Adsorption Isotherm and CO Adsorption. The plot in Figure 5, obtained in argon-saturated electrolyte, is similar to that obtained

by Will and Knorr[4] and by Böld and Breiter[5] by integration of slow periodic triangular potential-time sweeps. The abscissa of Figure 5 might alternatively be represented in units of the logarithm of hydrogen partial pressure (through the Nernst equation) and hence the plot is an experimental adsorption isotherm. Such isotherms have been studied in detail by Böld and Breiter,[5] who found that the apparent heat of adsorption of hydrogen decreases (irregularly) with increasing hydrogen coverage. Such an observation suggests heterogeneity of the surface. Such heterogeneity may generally be "original" (corresponding to such structural variations as imperfections, crystal orientation, etc.) or "induced" (caused by the very act of adsorption).

Figure 6 shows that the hydrogen coverage at any fixed potential drops off linearly with increasing time (and hence increasing coverage with CO, according to Figure 1) until high coverages are achieved. The empirical relationship followed for coverages less than approximately 0.75 of maximum is

$$\theta_H = (\theta_H)_0 \left[1 - \frac{\theta_{CO}}{1.15} \right] \qquad (3)$$

where θ_H is the fractional coverage with hydrogen atoms $= Q_H/_sQ_H$, $(\theta_H)_0 = \theta_H$ in absence of adsorbed CO, θ_{CO} is the fractional coverage with CO $= Q_{CO}/(Q_{CO})_M$, $(Q_{CO})_M$ is the charge corresponding to the maximum coverage with CO observed in this work $= 0.46$ mcoulomb/cm² (based on geometric surface area).

In the range of applicability of eq 3, we may conclude that the shape of the hydrogen adsorption isotherm

(4) F. Will and C. Knorr, *Z. Elektrochem.*, **64**, 258, 270 (1960).

(5) W. Böld and M. Breiter, *ibid.*, **64**, 897 (1960).

remains unchanged and that the effect of adsorbing CO is similar to a simple decrease in effective surface area for hydrogen adsorption. This contrasts with the conclusions of Breiter[6] for formic acid adsorption on Pt. According to Breiter, formic acid adsorbs on those sites having the highest heats of adsorption for hydrogen atoms and therefore preferentially blocks hydrogen adsorption at the higher potentials. The failure of CO to behave similarly on Rh may be due to either of the following possibilities.

(1) Appreciable variations in heats of hydrogen adsorption are "induced" (caused by the very act of adsorption) rather than "original" (e.g., corresponding to structural variations in sites), and similar induced heterogeneity occurs in the absence or presence of adsorbed CO.

(2) Sites having intrinsically (due to original heterogeneity) higher heats of adsorption for both hydrogen and CO do exist. However, under the conditions of diffusion-controlled CO adsorption, there is initially a random distribution of CO molecules on the surface.

No redistribution according to heats of adsorption occurs because of highly immobile adsorption. Since we are dealing with a polycrystalline sample, explanation 1 seems the less attractive one.

At values of $\theta_{CO} > 0.75$, analysis of Figures 1 and 6 reveals that θ_H drops off precipitously with increase of θ_{CO} at all potentials. This parallels the conversion from fast (diffusion controlled) to activated CO adsorption kinetics, and both phenomena may have a similar mechanistic origin.

(6) M. Breiter, *Electrochim. Acta*, **8**, 447 (1963).