JOURNAL OF CATALYSIS 46, 253-258 (1977)

The Role of Ultraviolet Radiation in Promoting the Palladium-Catalyzed Oxidation of Carbon Monoxide[1]

BOR-HER CHEN, J. S. CLOSE,[2] AND J. M. WHITE

Department of Chemistry, University of Texas, Austin, Texas 78712

Received April 5, 1976; revised October 25, 1976

The photoenhancement of the oxidation of carbon monoxide over palladium has been studied at low and high pressures in the temperature range 300–443 K. At a total pressure of 20 Torr there is a marked photoenhancement of the rate while at pressures below 10^{-4} Torr no enhancement was detectable. A correlation of these data and infrared spectroscopic data is established which suggests that a weakly bound state of CO is intimately involved in the photoenhancement process. The temperature dependence of the photoeffect is discussed.

I. INTRODUCTION

Photo-induced chemical reactions of chemisorbed species have been investigated on a variety of materials. On metals such effects are usually quite small (*1*) while on semiconductors, metal oxides for example, larger effects are frequently noted (*2*). Distinguishing primary quantum effects and radiant heating effects is often quite difficult, especially on metal substrates. The desorption of carbon monoxide from nickel may, using ultraviolet light of very low intensity, occur as a result of exciting directly the metal–CO bond but the cross section must lie below 10^{-21} cm^2 (*3–5*). On 304 stainless steel, photodesorption has been observed with the suggestion that a prominent role is played by the surface oxide which may be present (*6*).

An interesting photoeffect was reported by Baddour and Modell (*7*) in the carbon monoxide oxidation reaction over palladium They found, at 420 K, a 10-fold enhancement of the rate of production of CO_2 when light of wavelengths less than 300 nm illuminated a polycrystalline wire immersed in 6.1 Torr CO, 14.7 Torr O_2, and 740 Torr He. In other work from the same laboratory (*8*), irradiation, with ultraviolet light, of a platinum catalyst caused a decline in the rate of ethylene hydrogenation.

As a continuation of studies in this laboratory involving the low pressure oxidation of carbon monoxide over palladium (*9*) we have undertaken an extension to low pressures of the kind of experiment reported by Baddour and Modell (*7*). This paper reports the results of such experiments together with higher pressure experiments; the latter are in qualitative agreement with earlier work (*7*).

II. EXPERIMENTAL METHODS

The experiments reported here are conveniently divided into two groups, low pressure (10^{-5} Torr = 1.3×10^{-3} Pa) and

---

[1] Supported by the Office of Naval Research.

[2] Present address: Western Christian College, North Weyburn, Saskatchewan, Canada

ISSN 0021-9517

high pressure (20 Torr = 2.6×10^3 Pa). Each of these regions is presented separately in the experimental and results sections given below.

1. Pressures near 10^{-5} Torr (1.3×10^{-3} Pa)

The low pressure experiments were carried out in an UHV system similar to that described earlier (*9*). Substrates were polycrystalline Pd foils (99.99% purity) 0.013 mm thick with surfaces of about 4 cm^2. In some cases the substrate was Ar$^+$ bombarded and annealed and then heated for several hours at 900 K in about 10^{-4} Torr of oxygen. In other cases the Ar$^+$ bombardment step was omitted. No difference, within experimental error, was noted in the thermal CO oxidation rate over the two kinds of substrates. In the experiments involving light, Ar$^+$ bombardment was typically omitted.

Two light sources were used in these experiments. The first was a 200 W high pressure mercury arc lamp which is rich in ultraviolet intensity and includes many pressure broadened atomic mercury lines in its output. The unfiltered output of this source was used and enough power was absorbed by the substrate to increase the temperature from 300 to 330 K as measured with a thermocouple spot-welded to the substrate. Additional heating necessary to reach the desired operating temperature was supplied resistively.

The second light source was a low pressure mercury source, the output of which was concentrated at 254 and 185 nm. Although the intensity in these two lines was relatively high, the total output of the lamp caused no significant temperature rise in the sample (see Sec. IV). The radiation was transmitted through a Suprasil window in the vacuum wall.

To determine the influence of irradiation on the CO oxidation rate, a temperature was chosen and the steady state CO_2 production rate at that temperature was measured with and without irradiation. The total pressure was in the range 10^{-7}–10^{-4} Torr, the ratio of CO to O_2 was between 0.05 and 5.0, and the temperature was between 330 and 523 K.

The products were monitored using a small calibrated magnetic sector mass spectrometer mounted directly on the UHV system.

2. Pressures near 20 Torr (2.66×10^3 Pa)

A $0.013 \times 2.8 \times 3.3$ cm palladium foil, from the same lot used in the low pressure experiments, was mounted in the central part of a Pyrex cell (144.5 ± 0.8 cm^3) with a quartz window, parallel to the palladium sheet, closing one end. The cell was filled with known pressures of research grade CO and O_2 on a mercury-free oil-pumped vacuum line with a base pressure of 10^{-5} Pa. The reagents were passed through liquid nitrogen traps prior to entering the reaction cell.

The light source used in the experiment was the low pressure mercury arc described above but filtered through a Vycor plate. The filter removes 185 nm light making the output predominantly 254 nm radiation.

The reaction cell was heated in a constant temperature oven through which air was circulated. The temperatures ranged from 300 to 440 K in the experiments reported here. Using circular slits the light beam was spatially confined so that most of the beam struck the Pd foil. Through reflection, of course, the walls were unavoidably irradiated.

The reaction mixture, after a 12 hr experiment at some temperature, was analyzed by mass spectrometry. By careful manipulation with a Toepler pump–liquid nitrogen trap combination it was possible to separate the relatively small amount of CO_2 product from the CO and O_2. After separation the absolute amount of CO_2 was determined on a CEC 21-614 cycloidal mass spectrometer, the calibration of

TABLE 1

Carbon Dioxide Production

Label	Experiment	T/(K)				
		443	413	383	333	300
A	Blank, background	0.010	0.006	0.006	0.006	0.006
B	Irradiated, no catalyst	1.47[a] ± 0.05	0.85 ± 0.03	0.81 ± 0.03	1.06 ± 0.11	0.99 ± 0.07
C	Thermal, catalyst	1.11 ± 0.05	0.35 ± 0.03	0.32 ± 0.03	~0.006	~0.006
D	Irradiated, catalyst	4.06 ± 0.10	3.90 ± 0.11	2.02 ± 0.11	0.78 ± 0.11	0.60 ± 0.03
	Thermal production	0.55 ± 0.10	0.17 ± 0.10	0.15 ± 0.10	0.00 ± 0.10	0.00 ± 0.10
	Photoproduction	1.85 ± 0.11	2.92 ± 0.12	1.10 ± 0.12	−0.02 ± 0.16	0.00[b]

[a] Entries are in Torr ($\times 10^{-2}$) of CO_2 produced. The CO and O_2 pressures were fixed at 5 and 15 Torr, respectively.

[b] By assumption.

which was frequently checked. The rate was independent of irradiation times between 12 and 48 hr.

To determine the role of 254 nm radiation on the reaction rate, four experiments at each temperature were required: (A) a background experiment to determine the CO_2 in the starting materials, (B) a photolysis experiment with the palladium foil removed, (C) a thermal experiment with the palladium foil present, and (D) a photolysis experiment with the palladium foil present (see Table 1). Between each of the experiments the reaction vessel was evacuated to 10^{-4} Pa (10^{-6} Torr) and maintained at that pressure for 2 hr prior to refilling.

III. RESULTS

Under low pressure conditions, no detectable difference was observed under any circumstance between the rates of irradiated and nonirradiated experiments. The conditions of temperature span the range where the thermal CO_2 production rate is known to be both small and large (*9*a, b, *10*). Furthermore the CO and O_2 compositions span a range including both low and high (on the order of one monolayer) oxygen and carbon monoxide coverages (*9*c, d). Even when we operated at low temperatures around 350–380 K where the thermal rate is small but detectable, no change in rate on irradiation was observed for any CO/O_2 ratio in the range given above (the total pressure varied between 10^{-7} and 10^{-4} Torr).

In contrast to the low pressure data, the rates measured at high pressure were significantly larger when the system was irradiated, in qualitative agreement with the work of Baddour and Modell (*7*). Contrasting the low and high pressure data suggests a qualitative difference in the surface composition in the two situations.

In order to make the high pressure data semiquantitative we attempted to separate the photoinduced rate and the thermal rate, by means of the four measurements described in Sect. II. The results of these experiments are summarized in Table 1 for several temperatures. The entries give the pressures in Torr of CO_2 produced during a 12 hr period (measured in the 144.5 cm^3 vessel). The results point out clearly the enhancement of the reaction rate by irradiation. The experiments in which we irradiated the system without the catalyst present (Label B) always gave a significant amount of CO_2. This background production, which was not observed by Baddour and Modell (7), arises as a result of interactions occurring at the walls of the system. Various treatments of the walls changed the extent of this process but we were unable to reduce it to insignificance.

Since only one side of the palladium foil was irradiated, the rates to compare are the photorate on one side of the substrate with the thermal rate on one side of the substrate (with appropriate corrections for background and wall irradiation). Using the labels from Table 1, the thermal rate on one side of the substrate, R_T, is taken as

$$R_T = \tfrac{1}{2}[\mathrm{C}\text{–}\mathrm{A}]. \qquad (1)$$

The photorate, R_P, on one side of the substrate is:

$$R_P = \mathrm{D} - \mathrm{C} - b(\mathrm{B}\text{–}\mathrm{A}). \qquad (2)$$

According to Table 1, A is very small in all the experiments and makes little contribution to the results. In Eq. (2), a correction for the effect of irradiation on the walls has been made. This correction is only approximate and is based on two considerations. First, the total wall area illuminated in experiment B is about twice that irradiated in Experiment D because the palladium intercepts the light in the latter. Second, at low temperatures the amount of CO_2 produced in experiment B exceeds that produced in experiment D meaning the wall effect is smaller when the substrate is in place. At 383 K and above this correction makes only a small difference, but at 333 and 300 K, how this correction is made determines the overall result. We have assumed that at 300 K there is no photoeffect at the palladium substrate so that the photoinduced rate R_P must go to zero at this temperature. With this requirement the b-factor in Eq. (2) becomes 0.75. This factor, taken to be temperature independent, is then used to evaluate R_P at the other temperatures.

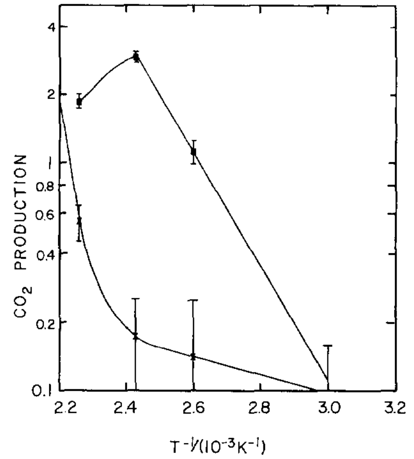

Fig. 1. Carbon dioxide production (Torr produced during a 12 hr experiment) vs the inverse of the temperature. (■) Photorate, (✕) thermal rate.

The last two lines in Table 1 list the photo and thermal production rates as calculated using Eqs. (1) and (2) and the results are plotted in Fig. 1. The uncertainties listed for the thermal data do not represent the reproducibility, rather our estimate of the long-term stability of the activity. The temperature dependence of these rates indicates a turnover in the photoinduced rate between 413 and 443 K. Between 333 and 413 the photorate shows an apparent activation energy of 45 kJ mole^{-1}. The thermal activation energy cannot be reliably estimated from the data because of uncertainty in the lower temperature data.

Two other experiments were carried out at 383 K. In the first 4.2 Torr of O_2 was introduced and irradiated and in the second 4.2 Torr of CO was irradiated. The production of CO_2 was not measurable in either experiment.

IV. DISCUSSION

There are two features of the photoenhancement on which attention is focused in this discussion; the pressure dependence and, at high pressures, the temperature dependence. Thermal activation energies have been measured in both the low and high pressure regimes. At pressures of a few Torr and above, reported activation energies lie between 93 and 178 kJ mole^{-1} (*7*, *11*, *12*). At pressures below 10^{-5} Torr, activation energies in the region where the CO pressure exceeds the O_2 pressure lie around 120 kJ mole^{-1} (*10*d). Thus, the overall activation energy for CO_2 production is not very sensitive to the CO pressure even though the CO coverage is expected to increase markedly in passing from 10^{-6} to 10 Torr.

In the experiments at high pressures involving irradiation, the molecular yields of CO_2 per incident photon can be estimated. The photon flux at 254 nm is about 2.5×10^{15} quanta sec^{-1} (*13*) from which we calculate the yield at 413 K to be 3×10^{-3}. Assuming momentarily that this quantum yield can be extrapolated into the low pressure regime, we estimate, based on the pumping characteristics of the flow system, a CO_2 pressure rise of 3×10^{-8} Torr which would be measurable under some conditions of our low pressure studies. Those studies involving the high pressure mercury arc which has intensity near 254 nm of about 1×10^{16} quanta sec^{-1} would produce an even higher pressure rise. Since no photoeffect was observed we conclude that the yield per incident photon at low pressures must lie below 5×10^{-5}.

Turning now to the high pressure photorates we note a fairly strong temperature dependence. Bulk heating can be eliminated using the arguments presented by Baddour and Modell (*7*). Thus, as they point out, the observed temperature dependence of the photoeffect must arise from changes in either the population of species which interact with the light or the population of species which react with the photoexcited species to form carbon dioxide, or both. Apparently this species is not present in significant concentrations when the total pressure is below 10^{-4} Torr, the CO/O_2 ratio lies in the range 0.05–5.0, and the temperature is higher than 333 K.

One clue regarding this species comes from spectroscopic studies done at relatively high pressure. While the infrared data from various laboratories (*14–16*) is not in good quantitative agreement, there is qualitative agreement as regards two general types of CO adsorption. One species rather weakly bound, exists in concentrations which are sensitive to both pressure and temperature. This species, which shows an infrared absorption band near 2100 cm^{-1}, can be removed, at least partially, by evacuation at room temperature or by heating at higher pressures. The other species is more tightly bound and exists on the surface in concentrations that are not strongly pressure dependent. This species, absorbing between 1900 and 1970 cm^{-1}, exists in concentrations on the surface which are temperature dependent, but below 473 K the data of Palazov *et al.* (*16*) indicates that little of the tightly bound CO is desorbed, even after prolonged evacuation. At some temperature between 413 and 493 K absorption due to the weakly bound CO disappears. Under working conditions, the data of Baddour *et al.* (*15*) indicate a significant depletion of the more strongly bound state between 375 and 400 K, but the weakly bound state is depleted even more.

Taking the above data into account, one possible interpretation of the low and high pressure photoeffect data centers on the weakly bound carbon monoxide state. Assuming its presence is required for there to be a photoenhancement, the absence of a photorate at low pressures and the presence of a photorate at high pressure and low temperature is understandable. This interpretation is compatible with what is known about low pressure CO adsorption/desorption. Flash desorption spectra (*9*a) show weakly bound and tightly bound CO species and above

430 K the weakly bound state will have a very small relative population. This model is also compatible with the observed decline in the photorate above 413 K, since it is in this temperature range that the weakly bound CO is readily removable at high pressure.

Qualitatively, our photodesorption data at high pressures are in agreement with comparable data reported by Baddour and Modell (*7*). As they point out, the photoeffect, and its temperature dependence, may arise from either the reaction of electronically excited CO or the desorption of CO. The quantitative details are, however, somewhat different; in particular we find an activation energy of 45 kJ mole^{-1} over the temperature range 330–413 K, whereas 90 kJ mole^{-1} is reported by Baddour and Modell (*7*) over the range 410–440 K. The reason for this difference is not understood and, while the role played by reactive and nonreactive oxygen (*17*) and other catalyst surface condition effects could be suggested, speculation about the source is not warranted.

CONCLUSIONS

On the basis of comparison of low and high pressure photoenhancement data with infrared, low pressure kinetic, and high pressure thermal data, we have been able to correlate the existence of the photoeffect with the presence of weakly bound carbon monoxide. The temperature dependence of the photoenhancement is discussed in terms of the temperature dependence of the amount of weakly bound CO and an activation energy requirement for a process occurring after photon absorption.

REFERENCES

1. (a) Adams, R. O., and Donaldson, E. E., *J. Chem. Phys.* **42,** 770 (1965); (b) Lange, W. J. *J. Vac. Sci. Technol,* **2, 74** (1961); (c) Brainare, J., PhD thesis, Washington State University, Pullman, Wash., 1968.

2. (a) Shapira, V., Cox, S. M., and Lichtman, D., *Surface Sci.* **50,** 503 (1975); (b) Badyaroy, S., Bottoms, W. R., and Mark P., *Surface Sci.* **28,** 517 (1971); (c) Freund, T., *J. Catal.* **3,** 289 (1964); (d) Lunsford, J. H., and Leland, T. W., Jr., *J. Phys. Chem.* **66,** 2591 (1962); (e) Cunningham, J., Kelly, J. J., and Penny, A. L., *J. Phys. Chem.* **75,** 617 (1971); (f) Tanaka, K. I., and Blyholder, G., *J. Phys. Chem.* **75,** 1037 (1971); (g) Steinbach, F., *Nature (London)* **215,** 152 (1967); (h) Doerffler, W., and Hauffe, K., *J. Catal.* **3,** 171 (1964).

3. McAllister, J. W., and White, J. M., *J. Chem. Phys.* **58,** 1496 (1973).

4. Genequand, P., *Surface Sci.* **25,** 643 (1971).

5. (a) Peavey, J., and Lichtman, D., *Surface Sci.* **27,** 649 (1971); (b) Moesta, H., and Breuer, H. D., *Naturwissenschaften* **55,** 650 (1968); (c) Moesta, H., and Trappen, N., *Naturwissenschaften* **57,** 38 (1970).

6. Fabel, G. W., Cox, S. M., and Lichtman, D., *Surface Sci.* **40,** 571 (1973).

7. Baddour, R. F., and Modell, M., *J. Phys. Chem.* **74,** 1392 (1970).

8. Aleksandrowicz, J., PhD thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1970.

9. (a) Close, J. S., and White, J. M., *J. Catal.* **36,** 185 (1975); (b) Matsushima, T., and White, J. M., *J. Catal.* **39,** 265 (1975); (c) Matsushima, T., Almy, D. B., Foyt, D. C., Close, J. S., and White, J. M., *J. Catal.* **39,** 277 (1975); (d) Matsushima, T., and White, J. M., *J. Catal.* **44,** 183 (1976); (e) Matsushima, T., Mussett, C. J., and White, J. M., *J. Catal.* **41,** 397 (1976).

10. (a) Ertl, G., and Rau, P., *Surface Sci.* **15,** 443 (1969); (b) Ertl, G., and Koch, J., *in* "Adsorption-Desorption Phenomena" (F. Ricca, Ed.), p. 345 Academic Press, New York, 1972; (c) Ertl, G., and Neumann, M., *Z. Phys. Chem. NF* **90,** 127 (1974). (d) Ertl, G., and Koch, J., *Proc. Int. Congr. Catal. 5th, 1972* p. 969 (1973).

11. Schwab, G. M., and Gossner, K., *Z. Phys. Chem.* **16,** 39 (1958).

12. Tajbl, D. G., Simons, J. B., and Carberry, J. J., *Ind. Eng. Chem. Fundam.* **5,** 171 (1966).

13. Bridges, L., PhD thesis, Univ. of Texas, Austin, Tex., 1973.

14. Eischens, R. P., Francis, S. A., and Pliskin, W. A., *J. Phys. Chem.* **60,** 194 (1956).

15. Baddour, R. F., Modell, M., and Heusser, U. K., *J. Phys. Chem.* **72,** 3621 (1968).

16. Palazov, A., Chang, C. C., and Kokes, R. J., *J. Catal.* **36,** 338 (1975).

17. Matuushima, T., and White, J. M., unpublished data.