

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

REDUCTION OF PALLADIUM OXIDE BY CARBON MONOXIDE¹

BY PAUL V. MCKINNEY

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In a previous article Taylor and McKinney² reported their observation that a sample of palladium oxide was not noticeably reduced by carbon monoxide at temperatures below 100°. Since oxide from the same preparation was reduced readily by hydrogen at 25° this fact appeared to be an exception to the generalization of Wright and Luff³ and the experiments of Fay, Seeker, Lane and Ferguson.⁴ A review of the data of these authors shows that in general carbon monoxide reduction starts at lower temperatures than the reduction with hydrogen in accordance with the heat of formation of water, and of carbon dioxide from the monoxide and oxygen.

In agreement with the conclusions of Langmuir⁵ concerning reactions producing heterogeneous solid phases,⁶ the reductions of copper oxide by hydrogen and by carbon monoxide have been classified as reactions at an interface.⁷ In contrast Benton and Emmett⁸ find that the reduction of ferric oxide by hydrogen has the characteristic properties of Langmuir's heterogeneous reactions resulting in the formation of solid solutions. In the former type the amount of reduction increases to a maximum while with the latter the rate decreases continuously with time. In the temperature range from 100 to 138° the reduction of palladium oxide starts rapidly but in the course of two hours falls off to negligible rates. Above 156° the reaction proceeds to completion. The effects of carbon dioxide and of oxygen on the reduction have been studied. In the case of copper oxide oxygen retarded the reduction, whereas at all temperatures it was found to increase the amount of palladium oxide reduced. Metallic copper is a catalyst for the combination of carbon monoxide and oxygen while palladium is not active toward this reaction.

Experimental Method

Purified carbon monoxide was passed at the rate of 22.8 cc. (0° and 760 mm.) per minute over a charge of 2.3 g. of palladium oxide and any carbon dioxide in the exit gas

¹ Acknowledgment is made to the Faculty of the Department of Chemistry of Princeton University for their courtesy in permitting the author the use of the facilities of the Frick Chemical Laboratory during the preliminary part of this investigation.

² Taylor and McKinney, *THIS JOURNAL*, **53**, 3604 (1931).

³ Wright and Luff, *J. Chem. Soc.*, **33**, 1, 504 (1878).

⁴ Fay, Seeker, Lane and Ferguson, *Polytechnic Engineer*, **10**, 72 (1910).

⁵ Langmuir, *THIS JOURNAL*, **38**, 2263 (1916).

⁶ Pease and Taylor, *ibid.*, **43**, 2179 (1921).

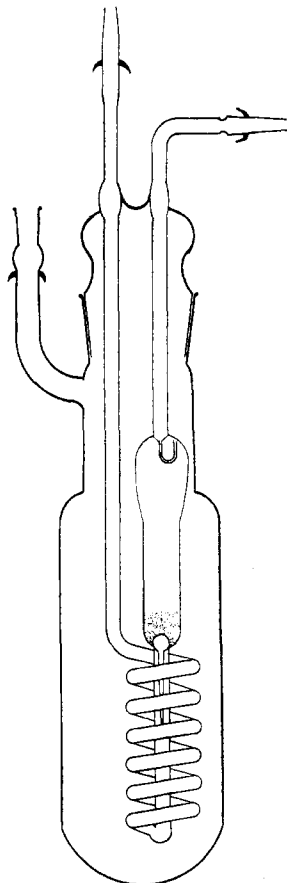
⁷ Jones and Taylor, *J. Phys. Chem.*, **27**, 623 (1923).

⁸ Benton and Emmett, *THIS JOURNAL*, **46**, 2728 (1924); Emmett, *Trans. Am. Electrochem. Soc.*, **51**, 207 (1927).

was determined. Palladium oxide was prepared from the chloride by the method of Shriner and Adams.⁹ Unless otherwise stated the entire apparatus and sample were flushed with nitrogen for two to five hours before each determination, the nitrogen being purified from traces of oxygen. Carbon monoxide was prepared by dropping formic acid on hot sulfuric acid, and was stored over water in a forty liter carboy from which it was forced by water pressure as desired. Any oxygen introduced by the water was removed by a copper furnace, the carbon dioxide absorbed by askarite and the gas dried by phosphorus pentoxide. An electrolytic generator was used to introduce oxygen into the gas stream. When carbon dioxide was desired the mixed gases were passed over heated copper.

Analysis.—The extent of reduction was followed in each case by analysis for carbon dioxide in the exit gas by one of the following methods. In the early experiments the carbon dioxide was absorbed in barium hydroxide in a special bottle with a Jena glass filter plate and spiral. The excess alkali was then titrated by standard hydrochloric acid. To eliminate the back pressure on the flowmeter due to the absorption bubbler the following *physical method* of analysis was devised. A trap of known volume was constructed and attached to a constant volume manometer. The exit gases from the reaction vessel were passed for a definite time through the trap cooled in liquid air. The carbon monoxide was quickly pumped off and the liquid air removed, allowing the pressure of the carbon dioxide in the known volume to be determined at room temperature. When this method proved too slow to follow the course of the reduction during the first fifteen minutes a *flow method* was arranged. The gas from the reaction vessel was passed through a large liquid air trap to remove carbon dioxide, then through a coil to warm it again to room temperature and through a second calibrated flowmeter. By this means the reduction was followed for each minute. The only difficulty experienced by condensing the carbon monoxide occurred when fresh liquid air was used inadvertently, *i. e.*, hour old liquid air from a compressor which had been running for several hours.

Apparatus.—The apparatus was completely glass sealed except for the rubber stoppers sealed with picein wax on the carboy and carbon monoxide and oxygen generators, and two ground-glass seals as noted below. In order to determine the possible effect of vapors from the vacuum stopcock grease or the paraffin oil used in the flowmeter one experiment at 100° was performed with liquid air surrounding a safety trap placed just before the reaction vessel. Since the results were identical with other runs at 100° this precaution was not subsequently observed. The fineness of the palladium oxide as a powder caused great difficulty in any method of supporting it on glass wool, asbestos or constrictions in the tube. The reaction vessel was then constructed as shown in the diagram using no other material than Pyrex glass. If there was a sudden surge of the gas when nitrogen or carbon mon-



⁹ Shriner and Adams, THIS JOURNAL, 46, 1683 (1924).

oxide was turned on or in changing from one analysis vessel or method to another, the wider expansion chamber above the charge allowed the powder to lift and release the pressure around itself. The fine jet at the top cut down the velocity of the gas flow in these sudden spurts, preventing the powder from being blown from the reaction vessel. The present design has several advantages over one recently described¹⁰ to overcome the same difficulties in that the unknown volume of gas in the region of the temperature fluctuations is less, the inert volume of the vessel is much less, ensuring more immediate removal of reaction products from the reaction vessel, and finally the reacting gas is preheated and except for channeling flows up around the entire charge. In addition interchangeable ground-glass seals were provided to connect the reaction vessel and also allow the introduction of the copper furnace between it and the flowmeter when carbon dioxide was desired.

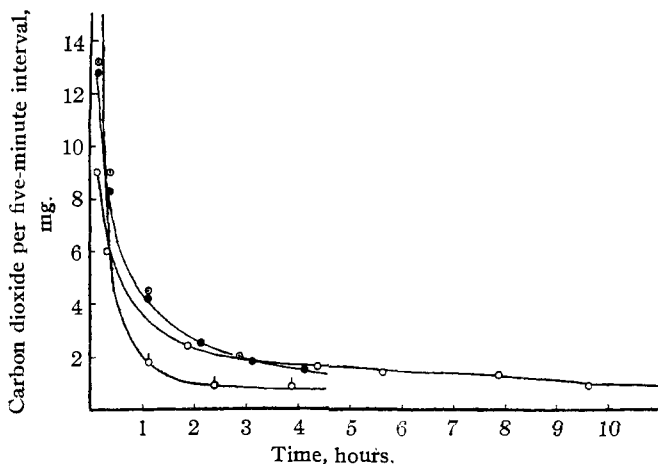


Fig. 1.—Reduction of palladium oxide at low temperatures; \circ , 100°; \bullet , 110°; \odot , 124°; \ominus , 138°.

Temperature of Reduction.—The direct reduction of palladium oxide at low temperatures where the reaction does not proceed to completion is given in Fig. 1. After the first period the reaction decreases very rapidly to negligible amounts. At 138° the charge was only half reduced after four hours. If this partially reduced material is heated to a higher temperature, the reduction increases but only becomes complete around 218°. The data for a sample first reduced at 100° are given in Table I. In the second column the time elapsed since the start of the reduction is given in hours, while in column three the duration of the individual measurement is stated. When the reduction is begun at 156° it proceeds to completion, the entire amount of carbon monoxide introduced reacting. Figure 2 shows the course of the reaction during the first fifteen minutes at this temperature.

In the present work nitrogen was used to sweep air from the apparatus in order to prevent a possible effect due to the catalytic reaction of carbon monoxide with oxygen on the surface of the oxide to be reduced. Since previous workers do not record having removed air from their apparatus before the passage of carbon monoxide, a sample of palladium oxide was examined in that manner. In order to detect the slightest reduction the absorption of carbon dioxide was continued thirty to forty-five minutes. This

¹⁰ Samuel Yuster, *J. Phys. Chem.*, **36**, 1056 (1932).

TABLE I

Temp., °C.	Time Elapsed, hours	Of expt.	CO ₂ , cc.	Cc./min.	Analysis method
100	0.2	10	6.1	.61	Phys.
	0.5	35	15.7	.45	Chem.
	1.0	45	11.7	.26	Chem.
	1.7	15	3.8	.25	Phys.
	2.0	(2.2 hrs.)	20.3		Chem.
	4.2	15	2.4	.16	Phys.
	5.5	15	2.1	.14	Phys.
	7.7	15	2.0	.13	Phys.
	9.5	15	1.3	.09	Phys.
	10.0	15	18.9	1.27	Phys.
156	10.2	15	13.8	0.92	Chem.
	11.0	15	6.5	.43	Phys.
	12.2	15	4.2	.28	Phys.
218	13.0	4	102.0	25.0	Phys.
	13.1	10	70.0	7.0	Chem.
	13.2	30	10.0	0.33	Chem.

sample produced carbon dioxide equivalent to 5.8 mg. per five-minute interval at 23°. When the apparatus was flushed with nitrogen for two hours prior to the determination, 4.5 mg. of carbon dioxide per five-minute interval was obtained. Reduction of carbon dioxide formation in each of these cases fell to negligible amounts after the second hour. Finally a sample of the oxide was heated with a stream of nitrogen passing over it for two hours at 156°. Carbon monoxide was then passed for two hours at 23° and no carbon dioxide could be detected. When this sample was heated to 56°, reduction could just be detected in one hour. At 76° it proceeded in measurable amounts. Although the reaction at 23° when the air is not first removed is probably due to adsorbed oxygen, there is also evidence for simultaneous reduction of the oxide since the color of the palladium oxide changes from chocolate-brown to black. In the last case above this did not occur until after the sample had been reducing for fifteen minutes at 76°.

Effect of Carbon Dioxide.—The rapid decrease in the rate of reduction below 156° suggested that a product of the reaction might be re-

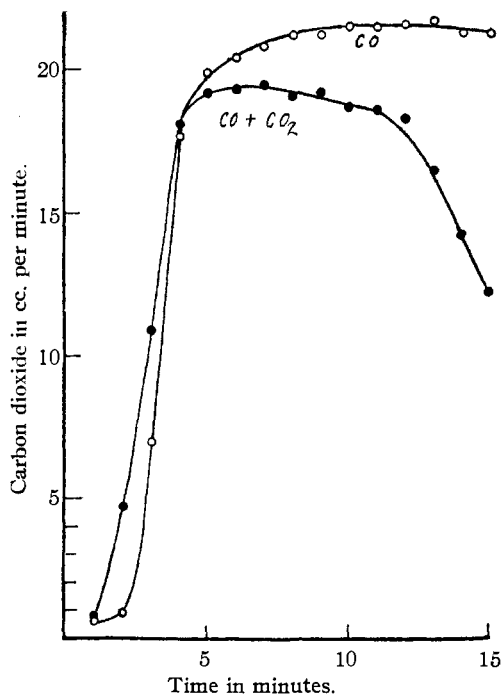


Fig. 2.—Effect of carbon dioxide on reduction at 156°.

tarding the further reaction; 2.8 cc. per minute of carbon dioxide was introduced into the stream of carbon monoxide by means of the electrolytic generator and copper furnace. Figure 2 presents the results, the small amount of carbon dioxide entirely inhibiting the reduction at 100° , no reaction being observed over a period of three hours. The reduction begins as usual at 156° in the presence of this amount of carbon dioxide but is retarded somewhat in the latter stages and as in the case of those reductions started at lower temperature does not appear to proceed to completion. This is quite similar to the result found for copper oxide and carbon monoxide by Jones and Taylor. Although not mentioned explicitly by them, the area under Curve V of their Fig. 3 is much less than that under Curve III for the unretarded reduction. These authors attribute the action

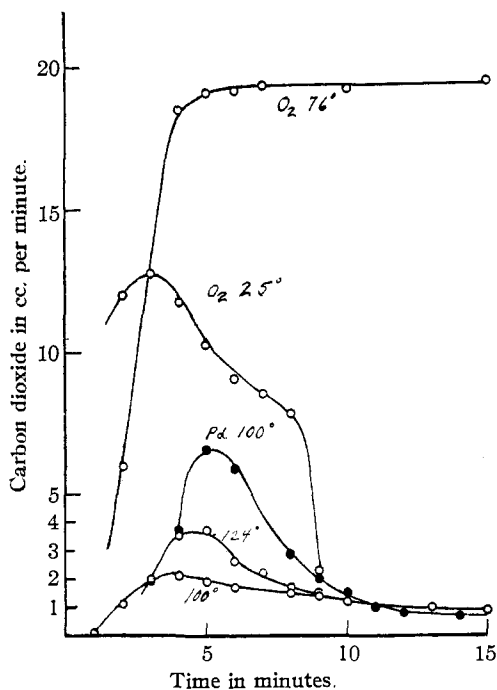


Fig. 3.

of carbon dioxide to its absorption by the unreduced copper oxide. The adsorptions on palladium oxide have not been determined.

Effect of Reduced Palladium.—The charge of completely reduced palladium was mixed with a fresh sample of the oxide and reduced at 100° . The reaction began slightly more rapidly but fell off in the same manner as normally, Fig. 3. This slight increase in the initial reduction may be an autocatalytic effect or it may equally be the effect of oxygen adsorbed on the palladium and not removed by the stream of nitrogen before beginning the reduction. Oxygen is strongly adsorbed on palladium; carbon dioxide is not.¹¹ In the reduction of NiO, Benton and Emmett found that the addition of freshly reduced nickel to a sample of nickel oxide did not appreciably affect the rate of reduction, although the reaction is autocatalytic. In the reduction of copper oxide the freshly reduced metal increased the reaction rate. The exact time at which the maximum reduction occurs cannot be significant because it was impossible to heat the charge instantly to the desired temperature. The watch was started at the moment the boiling bath was brought up about the reaction vessel.

Effect of Oxygen.—Oxygen was passed with the carbon monoxide at 100° . The rate of reduction increased immediately to the entire amount of carbon monoxide passing and continued to the complete reduction of the palladium oxide. This was surprising and a second sample was reduced at 76° in the same manner with oxygen present. Fig. 3; 1.4 cc. of oxygen was introduced and the carbon dioxide equivalent 2.8 cc. was subtracted in each case from the analysis data. There is also an increased reduction of the palladium oxide at 25° but it is not complete, soon falling off to negligible amounts.

Palladium oxide appears to catalyze the reaction of carbon monoxide with oxygen and the heat developed by this reaction is effective in causing the reduction of palladium

¹¹ Burns and Taylor, THIS JOURNAL, 43, 1274 (1921)

oxide. However carbon dioxide, or carbon monoxide itself, retards the reaction and the partially reduced Pd-PdO mixture is no longer effective to cause the combination of carbon monoxide and oxygen. The lowest temperature at which the combination of carbon monoxide and oxygen was observed over the completely reduced palladium was 218°.

Conclusion

The present results indicate that the reduction of palladium oxide occurs as an interfacial reaction. The very fineness of the palladium oxide as a powder is sufficient reason for the absence of an induction period. However, some process is strongly retarding the reaction at the interface since at the lower temperatures (100–124°) only 20% of the oxide is reduced before the reaction rate has decreased to negligible amounts. Probably carbon dioxide, the reaction product, is strongly adsorbed. This retarding action of carbon dioxide must necessarily occur from adsorption at the interface or on palladium oxide, since palladium was not found to adsorb it appreciably. Oxides in general adsorb carbon dioxide and water more than the metals. The adsorption of carbon monoxide is very strong on palladium, desorption increasing rapidly above 110°.

In order to show that the adsorption of carbon dioxide actually occurred, a sample of palladium oxide, 54% reduced, was flushed with nitrogen at room temperature. On raising the temperature, 3.8 cc. of carbon dioxide was evolved at 110° and 19.7 cc. at 218°. When carbon monoxide was passed over this sample at 110°, less than 1 cc. of carbon dioxide was evolved in thirty minutes but when flushed with nitrogen and again heated 12.6 cc. was evolved at 218°. These two cases represent an adsorption of approximately 60 and 40 volumes, respectively, per volume of palladium to be compared with an adsorption by completely reduced palladium, as measured by Taylor and Burns, of 14.4 volumes of carbon monoxide, 11.5 volumes of oxygen and 0.05 volume of carbon dioxide.

The action of oxygen in accelerating the reduction is difficult to explain, for although it is as strongly adsorbed on palladium as carbon monoxide, the two gases do not react on the metal at these temperatures. It is noteworthy that in all cases a large excess of carbon monoxide was present in the gas stream, and that if a partially reduced sample was allowed to remain open to the air for some time it then showed a preliminary increased evolution of carbon dioxide. The adsorptions on palladium oxide will be investigated.

Summary

1. A slight initial reduction of palladium oxide by carbon monoxide has been observed at 23°. If adsorbed oxygen is removed the reduction does not occur below 76°. Samples of the oxide have been reduced at 100, 110, 124, 138 and 156°. Below 156° the reduction does not proceed to completion but decreases in rate with time.

2. The presence of carbon dioxide in the stream of carbon monoxide

inhibits the reduction of palladium oxide at 100° and retards the completion of the reduction at 156°.

3. Oxygen in small amounts has been found to accelerate the reaction, causing complete reduction at 76°.

4. Palladium previously reduced from the oxide is only slightly autocatalytic toward the reduction. However, it is possible to consider that the reaction occurs at the interface and is retarded by strong adsorption of the product carbon dioxide on the oxide.

NEW BRUNSWICK, NEW JERSEY

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THE FREE ENERGIES AND HEATS OF FORMATION OF TETRAHYDRATE AND ANHYDROUS FORMS OF CADMIUM BROMIDE AND THEIR TRANSITION TEMPERATURES

BY HUGH M. SPENCER AND ROBERT F. SELDEN¹

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Introduction

In order that thermodynamic quantities may be fixed with the greatest possible exactness, it is necessary that they be determined by as many independent methods as are available. Spencer and Randall² in their theoretical treatment of cells involving the halides of silver, mercury, lead and cadmium tested the consistency of the various combinations involved by expressing the standard electromotive force of formation of the cadmium halides as determined through measurements of the electromotive force of formation of each of the other metallic salts of the same halogen and the metathetical relation of the halide and the corresponding cadmium halide. The standard electromotive force of formation³ is that of the reaction by which the compound is formed from the elements and water in their standard states.

The standard electromotive force of formation of cadmium bromide may be calculated through those of mercurous and silver bromides. At the time when the experimental work of the present paper was completed there existed the measurements of Oeholm⁴ on the cell

¹ Du Pont Fellow in Chemistry 1929-1930.

² H. M. Spencer and M. Randall, unpublished.

³ The use of this quantity rather than the electromotive force of formation from the elements in their standard states and water in the saturated solution is open to the objection that with the data available interpolations or extrapolations are required for obtaining the free energy of transfer of water from the standard state to the saturated solution in question, and uncertain quantities subject to revision are inserted. However, the same quantity is introduced in all summations for a given halide.

⁴ L. W. Oeholm, *Acta Soc. Sci. Fennicae*, **41**, 1 (1913).