Discussion of the Mechanism.—In the following experiments, only the concentration of oxalate ion was varied to produce the various desired conditions.

Above line L, Fig. 4, the color of permanganate was no longer visible. Since the "manganic-oxalate reaction" (reactions (10), (11) and (12)), was the only one taking place in this region, the rates were inversely proportional to the oxalate-ion concentration. Below L, however, permanganate was still present, but its effect differed throughout the series. In experiments (30) and (31), wherein the rate of reaction (11) was relatively low, reaction (8) took place at a rate depending directly upon the oxalate ion concentration, and upon the rate at which manganous ions were produced in reaction (11). These manganous ions reacted mainly as in equation (6) and not in equation (7). In experiments (33) and (34), however, reaction (11) was so rapid that the tetrapositive manganese ions produced as in equation (6) reacted mainly as in equation (7) and not in (8), in fact, the rate in (34) did not reach a maximum until all of the permanganate had been converted into the manganic state. If the permanganate–oxalate titration is carried out according to the directions of McBride, a process similar to that in experiment (34) will obtain. The permanency of the end-point is determined by the rate at which tetrapositive manganese, in equilibrium in reactions (6) and (7), reacts with water to form manganese dioxide.

Summary

The reaction between permanganate ion and oxalic acid has been studied and a mechanism developed which is in better accord with the results of experiments than those previously proposed. The reaction between the permanganate ion and oxalate ion was found to be extremely slow, while the reactions between tetrapositive manganese and oxalate ion and between tripositive manganese and oxalate ion proceed at a measurable rate. The tetrapositive manganese is present in equilibrium with permanganate, manganic and manganous ions, and a solution not containing initially any of the lower valent forms reacts but slowly, if at all, with oxalate. The mechanism adopted consists, when the concentration of manganous ion is low and that of oxalate ion is high, in the oxidation of the oxalate ion by tetrapositive manganese with the formation of the assumed intermediate ion CO_2^-, carbon dioxide, and manganic ion, the latter subsequently being reduced by the oxalate ion according to the mechanism given in a previous paper. When the concentration of manganous ion is somewhat higher, and that of the oxalate ion is lower, the oxalate ion is oxidized mainly by manganic ion. In the case of intermediate concentrations of manganous ion and oxalate ion, the latter is oxidized by both the tetra- and tripositive states of manganese.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Reduction of Platinum Oxide by Carbon Monoxide and Catalysis of the Reaction between Carbon Monoxide and Oxygen

BY PAUL V. MCKINNEY[1]

The interfacial characteristics of the reduction of metallic oxides in relation to Langmuir's[2] conclusions concerning heterogeneous reactions and the phase rule have been investigated by many.[3] Benton and Emmett described two types of reduction. That of nickel oxide occurred at an interface with an induction period and was autocatalytic. Iron oxide, which was known to form solid solutions on decomposition, was not found to reduce autocatalytically or with an induction period. According to Wöhler and Frey[4] the thermal decomposition of platinum oxide results in a solid solution with the lower oxide. If this also occurred at the temperature of reduction of the oxide, then by the reasoning of Benton and Emmett the reduction of platinum oxide should

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(1) At present with the Research Department, Phillips Petroleum Co., Bartlesville, Oklahoma.

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

(3) Benton and Emmett, *ibid.*, **46**, 2728 (1924); Larson and Smith, *ibid.*, **47**, 346 (1925); Pease and Taylor, *ibid.*, **43**, 2179 (1921); *Science*, **53**, 577 (1921); Jones and Taylor, *J. Phys. Chem.*, **27**, 623 (1923); Ubbelohde, *Trans. Faraday Soc.*, **29**, 532 (1933).

(4) Wöhler and Frey, *Z. Elektrochem.*, **15**, 129 (1909)

be similar to that of iron oxide. On the other hand, G. B. Taylor[5] and Starkweather in the reduction of copper oxide were able to obtain either type of reduction depending upon their methods of preparation of the sample and conditions of reduction. In the present work the reduction of platinum oxide was not similar in character to that of iron oxide, but was definitely autocatalytic in nature. The reduction occurred only after a definite induction period and with a maximum. In agreement with the latter authors this may be explained simply in the simultaneous formation of a large number of centers of reaction and in the liberation of large amounts of heat.

As in the reduction of palladium oxide[6] that of platinum oxide has been found to require a higher temperature when the reducing gas is carbon monoxide rather than hydrogen. Oxygen is an inhibitor to the process and carbon dioxide increases the length of the induction period. In contrast to the case of palladium oxide after the reaction has once begun carbon dioxide does not affect the reduction of platinum oxide. In this respect the retarding effect is similar to that of water vapor and carbon dioxide in the reduction of copper and nickel oxides. This may best be explained as due to the strength of adsorption of carbon monoxide on platinum and to a decreased adsorption of carbon dioxide on platinum oxide or at the interface as compared with palladium oxide.

Experimental

Materials.—The platinum oxide was prepared from chloroplatinic acid by the method of Voorhees and Adams.[7] It was a golden-brown powder. Adams and Shriner[8] proved its composition to be $PtO_2 \cdot H_2O$ and report that it appears amorphous under the microscope. Lunde[9] could obtain no interference lines in a Debye–Scherer diagram for the oxide obtained by dehydration at 200°. On heating no crystal form was obtained, the oxide decomposing to platinum and oxygen, with the lines of the former being observed above 600°.

Oxygen and nitrogen were obtained from commercial cylinders, the oxygen was merely passed over askarite and phosphorus pentoxide. The nitrogen was passed over copper at about 300° to remove oxygen and then over askarite and phosphorus pentoxide. Carbon monoxide was generated by dropping formic acid into concentrated sulfuric acid heated above 100°. It was stored over water and forced by water pressure as needed over calcium chloride and through the same purification system as with nitrogen. When carbon dioxide was desired either electrolytic oxygen produced at a known current rate or tank oxygen through a flowmeter was introduced into the carbon monoxide stream and led over reduced copper at about 175°.

Apparatus.—The purified gases were led through flowmeters calibrated for the gas for which it was used and then into a reaction vessel of the type previously described.[6] After a few experiments it was modified to admit a thermometer through the top with the bulb inserted to the middle of the charge. The exit gas passed through an askarite bulb and a coil to bring it back to room temperature. The unreacted carbon monoxide and/or other gas then passes through a flowmeter. A by-pass was provided to conduct the products directly from the reaction vessel through a barium hydroxide bubbler when desired. The latter was of the new Jena porous filter plate type and proved very efficient. Except for the pressure head necessary it proved almost as convenient as solid absorbents. A second by-pass permitted shunting any or all gases around the reaction vessel for analysis before a run, or during the attainment of temperature equilibrium.

Procedure.—In each experiment a sample of platinum oxide weighing about 1.5 g. was transferred from a desiccator to the reaction vessel and the latter sealed. It was dried in a stream of oxygen-free nitrogen at 110° for one hour and at 184° for thirty minutes using toluene and aniline vapor baths, respectively. The temperature was then reduced to 0° by an ice-bath and maintained there for another hour. Carbon monoxide was admitted at a flow rate of 20 cc. per minute or mixed with other gases in individual experiments.

Reduction.—When the platinum oxide was carefully dried in nitrogen or air no reaction was observed below 25°. At this temperature there was an induction period of two hours. In the next ten minutes the carbon monoxide reacting had increased from 0.4 cc. per minute to 0.8 cc. At the twelfth minute an explosion occurred as a result of the extremely rapid reaction of the entire flow of carbon monoxide. At 35 and 40° shorter induction periods were observed, followed by the same explosive type reaction, Table I. In all cases the transition from a slow reaction of less than 1 cc. of carbon monoxide reacting per minute to the rapid reaction of all the carbon monoxide was very abrupt. The time at which this rapid increase in reaction rate occurred was recorded as the end of the induction period.

The reduction is extremely sensitive to moisture. A sample dried at room temperature (26°) in nitrogen for three hours was reduced rapidly in the ice-bath after an induction period of only thirty-two minutes. When the carbon monoxide was bubbled through water and then passed over the well-dried sample a slight reaction (0.1 cc. of carbon dioxide per minute) was observed after fifteen minutes and rapid reaction began after fifty-five minutes. In the latter case the thermometer within the charge registered a gradual increase in temperature toward the end of the induction period. Probably the heat of reaction in the early stages at 0° is almost completely used in evaporation of the moisture condensed by the bath.

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(5) G. B. Taylor and Starkweather, THIS JOURNAL, **52**, 2314 (1930).

(6) McKinney, *ibid.*, **54**, 4498 (1932); **55**, 3626 (1933).

(7) Voorhees and Adams, *ibid.*, **44**, 1397 (1922).

(8) Adams and Shriner, *ibid.*, **45**, 2171 (1923).

(9) Lunde, *Z. anorg. allgem. Chem.*, **163**, 345 (1927).

There is a decrease in the length of the induction period when previously reduced platinum is mixed with the oxide, experiment 8. However, the effect is not nearly so great as in the case of copper and copper oxide.[3] In the present case the induction period at 40° decreased from twenty-nine minutes without the metal to twenty minutes. The powder was extremely fine and the individual granules through which a reaction zone or interface could spread were very small as compared with the 8–10 mesh granules of copper oxide.

Carbon dioxide in the stream of carbon monoxide lengthened the induction period at 40° from twenty-nine to sixty-five minutes, Table I. After the reaction had started no further effect was observed. In autocatalytic reactions it is not to be expected that a reaction product would inhibit the process.

TABLE I

REDUCTION OF PLATINUM OXIDE (PtO_2)

Samples of 1.5 g. with a flow of 20 cc. carbon monoxide per minute

Expt.	Sample: Preparation	Sample: Added	Temp., °C.	Induction period, minutes
10	Dried in N_2 110°		25	132
7	Dried in N_2 110°		35	27
5	Dried in N_2 110°		40	29
13	Dried in N_2 26°		0	32
15	Dried in N_2 110°	Moist CO	0	55
8	Dried in N_2 110°	Pt	40	20
9	Dried in N_2 110°	CO_2	40	65
2	Dried in N_2 25°	Fe	25	2
3	Undried	Fe	0	3

At the temperature of ordinary reduction of platinum oxide, the presence of 5 cc. of oxygen in a 20 cc. per minute flow of carbon monoxide prevents the reduction of the oxide. There is no reaction observable between the two gases up to 60° but above 70° reduction of the platinum oxide and complete reaction of the oxygen occurs. If the oxygen is in excess no reaction was observed to 70°. At 80° the carbon monoxide was completely burned but no reduction of the platinum oxide was observed. The effect of oxygen may be explained as due to a greater adsorption of oxygen on the oxide surface, preventing the access of carbon monoxide. The adsorption of the gases concerned on platinum has been reported and the adsorption on platinum oxide will be made.

A sample of platinum oxide made from chloroplatinic acid contaminated with 1% of iron was somewhat more readily reduced than pure platinum oxide. Reduction began immediately at 0° on an undried sample, in two minutes at 25° on an air-dried sample, and was observed at −10° in one case. An effect of slight traces of iron in the platinum oxide prepared for catalytic use has been observed by many authors and would seem to be paralleled by this increased ease of reduction.

PtO_2 as a Catalyst for the Reaction $CO + {}^1/_2\ O_2 \longrightarrow CO_2$.—The reaction of carbon monoxide and oxygen was determined at the surface of platinum oxide. If an excess of oxygen gas was used reaction was first detected at 70° after ten minutes, Table II. At 80° the entire 5 cc. of carbon monoxide in 15 cc. of oxygen reacted over 2 g. of catalyst. Only when the carbon monoxide–oxygen ratio was increased beyond equimolar quantities was the platinum oxide reduced. The catalytic reaction was examined in an excess of carbon monoxide with a fresh sample of platinum oxide, Table III. Darkening of the platinum oxide was first observed at 60° and reaction only became rapid above 80°. In all cases a large increase in temperature was observed as the reaction proceeded. From the last data of Table III it is evident that after the platinum oxide has all been reduced some reaction of the carbon monoxide with oxygen is still occurring. At that time it was observed that at the point where the gas mixture first came in contact with the platinum the latter was heated to glowing by the exothermic heat of the reaction. This glow at the one point seemingly represented the reaction of a large portion of the mixture. However, once the flow of gas was stopped and the platinum allowed to cool reaction did not occur at room temperature.

TABLE II

REACTION OF CARBON MONOXIDE AND OXYGEN

PtO_2 as Catalyst, Oxygen in Excess

Temp., °C.	Duration of test, minutes	The amount of gas is expressed in cc. per minute observed at end of test period: Reactants CO	Reactants O_2	Products Exit	Products CO_2
0	60	5	15	15	0
25	30	5	15	20	0
35	30	5	15	20	0
45	30	5	15	20	0
50	30	5	15	20	0
70	10	5	15	18.5	1
80	30	5	15	13	4.7
80	30	15	15	7.5	15
80	15	17	12	3.8	17
80	5	20	5	0	20
118	5	20	5	0	20
180	5	20	0	0	20
60	30	20	0	19	0

TABLE III

REACTION OF CARBON MONOXIDE AND OXYGEN

PtO_2 Reduced when the Monoxide is in Excess

Temp., °C.	Duration of test, minutes	The amount of gas is expressed in cc. per minute observed at end of test period: Reactants CO	Reactants O_2	Products Exit	Products CO_2
45	10	19.3	3.5	22.4	0.4
55	25	17.2	3.6	20.3	.5
60	15	17.5	3.5	20.4	.6
70	15	18.6	3.7	21.0	1.3
72	15	18.1	3.7	20.7	1.1
80	1	18.5	3.7	0	20.0
111	15	20.0	3.7	1.0	19.0
32	15	19.5	3.7	14.6	5.4
25	15	18.0	3.7	17.3	3.0

Platinum as a Catalyst for the Reaction $CO + {}^1/_2\ O_2$ CO_2.—The mechanism of this reaction on the surface of platinum foil was thoroughly investigated by Langmuir.[10] The platinum reduced by carbon monoxide is a black powder, which appears pyrophoric when exposed to air, as do many metals reduced by hydrogen. A sample of the oxide was completely reduced and cooled to 25°. When air was passed through this material the temperature

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(10) Langmuir, *Trans. Faraday Soc.*, **17**, 621 (1921).

momentarily rose to 50° and carbon dioxide was produced as indicated by the precipitate in a barium hydroxide solution. This is probably due to the combustion of the adsorbed carbon monoxide. As long as carbon monoxide is present in the gas stream the adsorption layer remains complete and reaction does not occur.

The lowest temperature at which combustion of a mixture of carbon monoxide and oxygen was observed over reduced platinum was 184°. The results are given in Table IV. The reaction becomes practically complete at 218° when oxygen is in excess. If the data of experiment 6 are calculated in the usual Arrhenius formula the activation energy for the combustion, as catalyzed by the platinum black, is 23.7 kg. cal. This may be compared with a value of 27.4 kg. cal. calculated for the same temperature from the data of Langmuir on platinum foil. With an excess of carbon monoxide very little reaction was observed even at 218°.

The data of experiment four are included for comparison. The catalyst in this case contained 1% of iron in the original chloroplatinic acid from which the platinum oxide was prepared. This sample was much less readily sintered at 218° than were the pure samples. At 218° all samples slowly change from the black powder to a gray spongy appearance. This process of sintering is often decreased by the presence of inert materials.

TABLE IV

REACTION OF CARBON MONOXIDE AND OXYGEN

Reduced platinum as catalyst, gas flow in cc. per minute

Expt.	Temp., °C.	CO, cc.	O_2, cc.	CO_2, cc.	Length of test, minutes
		Excess Oxygen			
4	184	2.8	4.5	2.2	20
4		2.6	8.0	2.6	20
6		4.0	20.0	0.7	30
6	218	5.5	19.0	4.3	30
		5.2	18.7	5.1	30
		Excess Carbon Monoxide			
4	184	20	2.5	0	
4	218	20	2.2	1.0	
6	218	20	4.5	1.1	

Discussion

One outstanding characteristic of the reduction of platinum oxide is the suddenness of the start of the reaction. In the last two or three minutes of the induction period the rate of reaction may be observed to increase from 0.1 cc. of the 20 cc. flow of carbon monoxide to as much as 1 cc. per minute. In the next instant the reaction will have become complete. In several cases the expansion following the reaction was so great that it shattered the reaction vessel. Apparently the reaction starts at the same time on most of the grains of very finely powdered oxide. The process is extremely exothermic. Temperature increases as great as 80 to 100° in five minutes due to the reduction have been observed. This temperature increase is itself sufficient in this case to account for the autocatalytic nature of the reaction.

The effect of oxygen is certainly that of preventing the formation of the original reaction centers from which the reduction spreads. Since carbon dioxide also exerts an inhibiting effect upon the initial reduction a large adsorption of this gas on platinum oxide will be expected. The effect of moisture must be related to the existence of the hydrate $PtO_2 \cdot H_2O$ and is evidence for a strong adsorption of water vapor. In the same manner the presence of iron oxide as an impurity must form active irregularities in the oxide at which the reduction starts. The lowest temperature of reduction of iron oxide is at least 100° higher than the temperature of the present process.

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Summary

1. The reduction of well-dried platinum oxide (PtO_2) by carbon monoxide occurs at 25° with an induction period of two hours. The latter is reduced to thirty minutes at 40°. The process is extremely autocatalytic. At the end of the induction period the reaction quickly reaches explosive proportions. The reaction is highly exothermic.

2. If the platinum oxide is not dried at 110° or if moist carbon monoxide is used reduction occurs at 0° with a short induction period.

3. The presence of iron in the salt from which the oxide is prepared accelerates the reduction.

4. Platinum oxide is a catalyst to the combustion of carbon monoxide at 80° and is not reduced so long as oxygen is in excess.

5. Platinum black prepared from the oxide by reduction in carbon monoxide is a catalyst to the combustion of carbon monoxide. With oxygen in excess reaction was observed at 184° and became complete at 218°. With excess carbon monoxide only a trace of reaction was observed at 218°.

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