rium $5B_2H_6 + 2BCl_3 \rightleftarrows 6B_2H_5Cl$ was established, very much in favor of chlorodiborane. Then the sample was distilled through a U-tube at −150°, in which all substances less volatile than diborane were trapped. The chlorodiborane was freed from pentaborane, tetraborane and the probable constant-boiling mixture of boron trichloride and chlorodiborane, by several slow distillations through a U-tube at −120°. After each distillation it was necessary to heat and evacuate the tubes in which the boron trichloride was condensed, in order to remove adsorbed traces of this impurity. The diborane was entirely removed by distillation through a U-tube at −140°, in which nearly all of the chlorodiborane was condensed. At length there was obtained a 4-cc. (gas) sample having a vapor tension of 18 mm. at −78.5°; further repetition of the process of distillation gave the same result, and the value was also found to be independent of the volume of the measuring tube. The compound was so unstable that the vapor tension measurement had to be made within a period of twenty seconds.[8] During the measurement, enough decomposition occurred that a repetition of the measurement after complete recondensation showed an increase to 19 mm. The fact that the increase was observed only after complete recondensation shows that the decomposition occurred mainly in the vapor phase, part of which was at room temperature. It was not found possible to obtain a trustworthy set of vapor tensions at temperatures other than −78.5°. The melting point was measured by the use of the magnetic device of Stock[9] and the ethylene vapor tension thermometer.[10] It was found to be sharp, at −142.0°. The combined evidence of the recurring 18 mm. vapor tension and the sharp, reproducible melting point, is sufficient to establish, beyond reasonable doubt, the uniformity of the substance.

The substance was analyzed by passing the measured sample (3.68 cc. of gas) through a hot quartz tube, measuring the volumes of the resulting hydrogen, boron trichloride, and hydrogen chloride, and weighing the boron. The resulting analytical formula was $B_{1.8}H_{6.1}Cl_{0.95}$. A low value for boron was to be expected.

Summary

The isolation of the exceedingly unstable substance chlorodiborane (m. p. −142°; vapor tension at −78.5°, 18 mm.) is described.

Some modifications and additions to the high vacuum methods developed by Stock for handling highly volatile substances are given. These include a simplified technique of fractional condensation, new designs for the float valves and the application of fractionating columns.

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(8) *This time was ample, because of the thin, flat bottom of the* tube, and the extremely small liquid volume of the sample (about 0.01 cc.). Measurements on similar quantities of stable substances have shown that equilibrium actually is reached in ten seconds if the bath used is an ether suspension of solid carbon dioxide in equilibrium with its vapor at one atmosphere pressure.

(9) Stock, *Ber.*, **50**, 156 (1917).

(10) Stock, *Z. Elektrochem.*, **29**, 354 (1923).

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The Oxidation of Carbon Monoxide with a Silver Catalyst

BY ARTHUR F. BENTON AND RICHMOND T. BELL

The myriad studies of kinetics in contact catalysis have thrown much light on the problem but have so far failed to furnish an adequate picture of the processes involved. Kinetics have almost invariably been interpreted in terms of arbitrarily assumed adsorptions—a method which is notoriously fallible. Examples of the progress that may be anticipated from parallel studies of adsorption and catalysis on the same material are furnished by the investigations of Pease and coworkers[1] on the ethylene-hydrogen combination in contact with copper and other metals, and of Benton and Elgin[2] on the synthesis of water with silver and gold catalysts. The methods employed by the latter have now been applied to the oxidation of carbon monoxide in presence of finely-divided silver. This reaction has proved to be unusually simple, since it is not retarded by the reaction product and since only one of the reactants, oxygen, is much adsorbed by the catalyst.

The union of carbon monoxide and oxygen has been studied in numerous previous investigations, particularly with oxide catalysts and with platinum. Bone and Andrew[3] used several other metals, including gold gauze. No previous parallel study of adsorption and catalytic activity for this reaction has been made under conditions which permit a quantitative examination of its molecular statistics.

Method and Materials

Apparatus.—The "flow" method, essentially as described by Benton and Elgin,[2a] was employed. Measured propor-

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(1) Pease, THIS JOURNAL, **45**, 1196, 2235, 2296 (1923); Pease and Stewart, *ibid.*, **47**, 1235 (1925); **49**, 2783 (1927); Pease and Harris, *ibid.*, **49**, 2503 (1927).

(2) Benton and Elgin, (a) *ibid.*, **48**, 3027 (1926); (b) *ibid.*, **49**, 2426 (1927); (c) *ibid.*, **51**, 7 (1929).

(3) Bone and Andrew, *Proc. Roy. Soc.* (London), **A109**, 459 (1925); **A110**, 16 (1926).

tions of carbon monoxide and oxygen, and occasionally carbon dioxide, were passed over the catalyst at atmospheric pressure and at a total rate of 50 cc. (0°, 760 mm.) per min. Rates of reaction were determined by absorbing the effluent carbon dioxide in glass-stoppered weighing tubes filled with "Ascarite."

To avoid the serious temperature gradients which were found to exist through an active catalyst confined in a glass tube, the catalyst chamber was constructed of heavy-walled brass tubing 2.2 cm. in inside diameter, closed at both ends with threaded heads. One of these carried centrally a brass thermocouple well 0.9 cm. in outside diameter. The brass tubes for gas inflow and outflow, threaded into the heads, were welded to short copper tubes, the latter being in turn connected to glass tubes by copper–glass seals. The chamber was heated in a horizontal position by a cylindrical electric furnace so wound as to furnish a uniform temperature over the middle 8 cm., which is about five times the length of catalyst employed. Temperatures were measured potentiometrically with a calibrated iron-constantan thermocouple. With the relatively inactive catalyst finally used no difference in temperature was ever detected within the catalyst bed. The empty catalyst chamber, after cleaning with acetone, ether, hydrochloric acid and distilled water, showed no catalytic effect on mixtures of carbon monoxide and oxygen at 150°, and almost none at 175°.

Gases.—Carbon monoxide from a well-swept out generator containing potassium ferrocyanide and concentrated sulfuric acid was washed with strong potassium hydroxide and stored over water in a carboy under pressure. Thence it passed to the catalyst over heated platinized asbestos, soda-lime, calcium chloride and phosphorus pentoxide. Oxygen was obtained electrolytically from carbonate-free sodium hydroxide solution, and freed in the usual manner from hydrogen and water. Carbon dioxide was introduced when desired by adding to the monoxide stream the calculated quantity of oxygen and converting over a gently heated mixture of copper oxide and manganese dioxide; blank tests before every such run showed complete conversion of the oxygen to carbon dioxide. Additional oxygen, to be studied as such, was introduced between this point and the catalyst chamber.

Catalyst.—The preparation of the catalyst and its intentional deactivation by long heating at 300° have been described by Benton and Drake.[4] Of the product obtained a representative sample of 4.2815 g. was used in these catalytic experiments; the remaining 39.4 g. was used in the adsorption studies here reported, and was the same sample whose behavior in contact with oxygen was later investigated by Benton and Drake, who designated it Ag_1. The catalyst, held in place with glass wool, occupied a length of 1.7 cm. in the annular space surrounding the thermocouple well.

To obviate any possible cumulative effect of the strongly adsorbed oxygen, a uniform procedure was adopted consisting in passage of pure carbon monoxide over the catalyst for one-half to one hour before and after each run, at the temperature of the catalysis. Thus each run was started with a presumably bare silver surface.

Reaction Kinetics

Experimental Data.—All experiments are numbered in the order in which they were made. About every second or third run was a "check run," to test the constancy of the activity of the catalyst. These were always made at 80° with a 9:1 mixture of carbon monoxide and oxygen. All experiments with mixtures containing excess of monoxide were made first. The check runs during this period (Runs 36–49) showed remarkable agreement, the average deviation being 0.5% and the maximum 1%. After the first run with excess of oxygen (Run 53), the next "standard" run showed a slightly but definitely decreased activity, from 2.80 to 2.57 mg. of carbon dioxide per minute. Thereafter an almost negligible decrease in activity occurred, the average deviation from the mean of 2.48 being 2.5% and the maximum 4.5%.

The kinetics of reaction have been derived by use of the average partial pressures of the entering and exit gases. This method, which has been shown[5] to be reliable for conversions up to 50%, involves no appreciable error in these measurements, since the conversion never exceeded 17%. Average partial pressures are denoted $\bar{p}$. The experimental results for mixtures containing an excess of carbon monoxide are given in Table I, and those with an excess of oxygen in Table II. In each case Columns 3 and 4 give the number of cc. at 0°, 760 mm., of carbon monoxide and dioxide, respectively, entering the catalyst per minute. The remainder of the 50 cc. was oxygen. Each value of the yield of carbon dioxide Y produced by reaction represents the average of about seven weighings, each to 0.1 mg., made successively after attainment of the steady state. The average deviation of the individual values from the mean was in general less than 0.1 mg. The values of k in the last column are the reaction velocity constants calculated from the equation $Y = k\bar{p}_{CO}$.

Conclusions.—The results in Table I show that a variation of the oxygen pressure by a factor of eight is without effect on the rate of reaction. Further, the rate was not sensibly influenced by concentrations of carbon dioxide as high as 10%. The results in Table II confirm the inertness of the reaction product. They show, however, that the rate is very closely proportional to the pressure of carbon monoxide. In each table the

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[4] Benton and Drake, This Journal, 56, 255 (1934).

[5] Benton, *Ind. Eng. Chem.*, 19, 494 (1927).

reaction constant $k(= Y/\bar{p}_{CO})$ is constant within the limits of experimental uncertainty, but is nevertheless about four times as great with excess oxygen as with excess carbon monoxide.

A plot of log k vs. $1/T$ is shown in Fig. 1, based on the average values of the velocity constants from Tables I (excess CO) and II (excess O_2). In the latter case it will be observed that the apparent energy of activation increases with the temperature. The values in kcal. calculated from point to point are: 80–100°, 11.4; 100–120°, 13.3; 120–140°, 15.2. The average is 13.3. With excess carbon monoxide at 80–100°, E = 13.1.

TABLE I

REACTION KINETICS. EXCESS CARBON MONOXIDE

Temp., °C.	Run no.	CO, cc./min.	CO_2, cc./min.	$\bar{p}_{CO}$, mm.	Y, mg./20 min.	$k \times 10^2$ mg./20 min./mm.
80.0	36–49	45	..	675	2.80	0.415
	37	47.5	..	714	3.10	.434
	39	48.75	..	735	3.15	.428
	41	49.38	..	745	3.04	.408
80.0	50[a]	41.88	5.00	651	2.76	.424
	51[b]	47.5	2.50	712	3.04	.427
	52	47.5	1.25	711	3.10	.435
100.0	43	45.0	..	674	7.45	1.105
	45	47.5	..	709	8.20	1.157
	47	48.75	..	724	8.48	1.170
	48	49.38	..	739	8.53	1.153

[a] Total flow = 48.13 cc./min. [b] Total flow = 50.63 cc./min.

TABLE II

REACTION KINETICS. EXCESS OXYGEN

Temp., °C.	Run no.	CO, cc./min.	CO_2, cc./min.	$\bar{p}_{CO}$, mm.	Y, mg./20 min.	$k \times 10^2$ mg./20 min./mm.
80.0	68	5.0	...	74.9	1.50	2.00
	70	10.0	...	152.5	2.85	1.87
100.0	59	2.5	...	37.3	1.77	4.75
	57	5.0	...	75.1	3.51	4.67
	55	7.5	...	112.8	5.00	4.44
	53	10.0	...	149.9	6.90	4.60
100.0	67	7.5	2.5	111.9	4.88	4.36
	72	10.0	0.5	149.4	6.84	4.57
120.0	60	2.5	...	36.8	4.42	12.02
	61	5.0	...	73.6	8.61	11.70
	63	7.5	...	110.5	11.80	10.68
	64	10.0	...	147.5	16.83	11.40
140.0	74	5.0	...	71.0	20.83	29.35
	76	10.0	...	143.2	41.81	29.20

Adsorption by the Catalyst Material.—Adsorptions were studied with a 39.4-g. sample of the identical material used for catalysis. The apparatus was similar to that described by Benton and White.[6] The free space was determined at 0, 80 and 140° with nitrogen, which is known not to be measurably adsorbed in this range. In all cases the unit of adsorption is cc. at 0°, 760 mm., per 39.4 g. of silver.

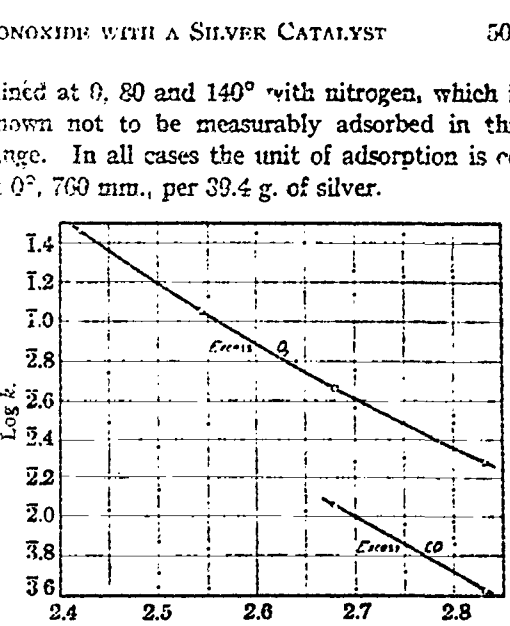

Fig. 1.—Rate of reaction as function of temperature.

The results with carbon monoxide at 0 and 140° are shown in Fig. 2. The adsorptions are for the most part of the physical type, but extrapolation to zero pressure of the curve for 140° suggests that an activated adsorption of 0.15 cc. may have occurred. From the curves as drawn the calculated heat of adsorption is 2.3 kcal. for an adsorption of 0.31 cc. and 2.6 for 0.56 cc. If 0.15 cc. of possible activated adsorption is subtracted from the observed values at 140°, the corresponding heats are 3.4 and 3.1 kcal. A value of about 3 kcal., which is roughly twice the heat of vaporization, is to be expected for a physical adsorption of carbon monoxide.

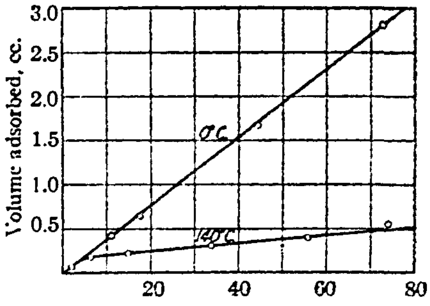

Fig. 2.—Adsorption of carbon monoxide.

The adsorption of carbon dioxide at 0° and 1 atm. amounted to 0.5 cc. At 140° there was no measurable adsorption, the carbon dioxide and nitrogen values agreeing at all pressures within ±0.03 cc. With both carbon monoxide and

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[6] Benton and White, THIS JOURNAL, 52, 2325 (1930).

dioxide equilibrium was established practically instantaneously.

The slow sorptions of oxygen measured at 80 and 140° need not be detailed here, in view of the more elaborate study subsequently made by Benton and Drake[4] on the same sample. They showed that at 1 atm. oxygen first reacted to form silver oxide at a measurable rate at about 100–140°. The rate of activated adsorption of oxygen was very much greater under all conditions than the rate of oxide formation. Of the maximum activated adsorption of 3.5 cc., the first cc. was taken up quickly even at −78°; the remainder was adsorbed at rates which increased rapidly with rising temperature (activation energy = 12.7 kcal.), but which decreased regularly at a given temperature with increasing extent of adsorption. The *initial* rate on the bare surface was of the same order as that calculated on the assumption that every collision of gaseous oxygen with the surface, in which the joint energy exceeded 12.7 kcal., resulted in activated adsorption. These authors have also found[7] that, unlike a bare surface, a silver surface more or less occupied by oxygen in form of activated adsorption is capable of adsorbing slowly an almost equal quantity of carbon dioxide. However, since this last process was slow even at 197° it is hardly possible that it was a significant factor at the temperatures used in catalysis, 80–140°.

Reaction Mechanism

Oxide Formation not a Factor.—From the measurements of Benton and Drake[4] it follows that at the highest temperature and the highest oxygen pressure used in catalysis the maximum, initial rate of oxide formation by the 4.28 g. of catalyst was equivalent to only 0.062 mg. of carbon dioxide per twenty minutes. The observed catalytic rates were 300–600 times greater. If the oxide did not react at all with carbon monoxide the total amount accumulated in a three-hour run would not exceed the equivalent of 0.15 cc. of oxygen. Since the energy of activation for oxide formation is nearly twice that for the catalytic reaction of the monoxide, the possible significance of oxide formation as a factor in the catalysis becomes still more remote at lower temperatures.

Rate of Adsorption Compared with Catalysis.—The catalytic reaction clearly consists of two steps, (1) activated adsorption of oxygen, followed by (2) reaction of adsorbed oxygen with carbon monoxide when the latter impinges on it from the gas phase, or becomes adsorbed on top of or adjacent to the oxygen. Contrary to the common assumption in such cases, neither step can be said to be fast compared to the other. At the start of a catalytic experiment oxygen is taken up by the bare surface much more rapidly than it is removed by carbon monoxide. The resulting accumulation of adsorbed oxygen causes a decrease in the rate at which further oxygen is adsorbed and an increase in the rate of its removal by the monoxide. Finally, when the steady state is reached, these two rates must become equal, since at 80–140° oxygen leaves the surface *only* by reaction with carbon monoxide. The measurements of Benton and Drake, after division by the factor 9.2 to make them applicable to the smaller sample used in catalysis, give the values shown in Table III for the rate of adsorption of oxygen at 100°. The adsorption intervals in Column 1 are for the larger sample, not for the catalyst. The last three columns state the equivalent rate of formation of carbon dioxide corresponding to reaction of each oxygen as fast as it is adsorbed. The three pressures of oxygen there listed are, respectively, the lowest and highest partial pressures used in catalysis with excess carbon monoxide and the highest pressure with excess oxygen. The first cc. was adsorbed practically instantaneously even at −78°. Comparison of these values with the catalytic yields Y in Tables I and II shows that only the first cc. of the possible 3.5 is adsorbed rapidly enough to account for the rate of catalysis with excess carbon monoxide; with mixtures containing excess of oxygen the adsorption at the steady state can reach about 1.2 to 1.4 cc. (equivalent to 35–40% covering of the surface), depending on the pressure of the monoxide. These conclusions also hold for temperatures other than 100°, since the activation energies for adsorption and for reaction with carbon monoxide are nearly equal. Thus at equal

TABLE III

RATE OF ADSORPTION OF OXYGEN AT 100°

Adsorption, cc.	Rate × 10^3 cc./hr./mm.	Rate, equiv. mg. CO_2/20 min.		
		pO_2 (mm.) = 10	75	700
1.0–1.2	24	0.32	2.4	22
1.2–1.4	4.1	.055	0.41	3.8
1.4–1.6	0.74	.0099	.074	0.69
1.8–2.0	.18	.0024	.018	.17
2.2–2.4	.028	.00037	.0028	.026
2.4–3.0	.013	.00017	.0013	.012

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(7) Drake and Benton, forthcoming contribution.

partial pressures the steady-state adsorption of oxygen should be independent of the temperature, so that the "apparent" and "true" activation energies are the same.

If all the adsorbed oxygen had equal reactivity, a 20–40% greater specific rate would thus be expected in presence of excess oxygen than in presence of excess carbon monoxide. The observed ratio of these specific rates was 4.6 at 80° and 4.0 at 100°. When corrected for the slight intervening change in the activity of the catalyst, the ratios become 5.1 and 4.5. These facts, together with the somewhat smaller activation energy with excess oxygen, suggest the possibility that the first cc. of oxygen adsorbed is not the most reactive, and takes a prominent part in the mechanism only because of its extremely high rate of adsorption. A direct test of this possibility will be attempted.

Test of Collision Mechanism.—On the hypothesis, possibly over-simplified, that carbon dioxide is formed at every collision of monoxide with adsorbed oxygen in which the joint energy exceeds the energy of activation, the theoretical rates of reaction can be calculated as follows. On the various assumptions that activated adsorption involves one molecule of oxygen to one, two or four superficial silver atoms,[4] the areas presented by the oxygen adsorbed by the catalyst at the steady state are calculated to be within the limits 2.4×10^3 and 13.4×10^3 sq. cm. At 100° and 1 mm. carbon monoxide would strike these surfaces with the necessary activation energy (13.3 kcal.) at rates equivalent to the formation of 1.2 to 6.6 mg./carbon dioxide per twenty minutes. The observed specific rates of reaction (0.0115 and 0.046 with excess monoxide and oxygen, respectively) are smaller by factors varying from 30 to 600. Even with the lower figure, confirmation of the simple collision hypothesis would require an activation energy of 15.9 kcal. It is conceivable that in some way not now clear a variation of activation energy with the amount of oxygen adsorbed might resolve this discrepancy. Unfortunately, alternative hypotheses as to the reaction mechanism, such as the requirement that carbon monoxide be adsorbed on top of or adjacent to the adsorbed oxygen, cannot be tested quantitatively with the information at present available.

Summary

A study in flow system of the kinetics of oxidation of carbon monoxide with a reduced silver catalyst in the range 80–140°, together with the adsorptions of the three gases involved, has led to the following results.

The rate of reaction is proportional to the pressure of carbon monoxide and independent of that of the dioxide. It is independent of the oxygen pressure when carbon monoxide is present in excess. With mixtures containing excess of oxygen the specific reaction rate, that is, the rate per unit pressure of monoxide, is about five times as fast as for mixtures with excess of monoxide. The average energy of activation is 13.3 kcal.

These facts are shown to be reconcilable with the adsorption measurements in the same range of temperature, which exhibit a very small adsorption of carbon monoxide, none of dioxide, and a slow, irreversible, activated adsorption of oxygen. The maximum rate of formation of silver oxide is negligibly slow compared to the rates of adsorption and catalysis. The rates of adsorption of oxygen are sufficient to keep the surface 30–40% covered in the catalysis.

The observed rates of reaction are at least 30 times less than those calculated on the assumption that reaction occurs at every collision of gaseous carbon monoxide with adsorbed oxygen, in which the joint energy exceeds the energy of activation.

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