Kinetics of the Isotopic Exchange Reaction between Carbon Monoxide and Carbon Dioxide*

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(Received November 5, 1952)

Introduction

The kinetics of the exchange reaction between carbon monoxide and carbon dioxide have been investigated by Brandner and Urey,(1) using natural C^{13} isotope as a tracer, and by Norris and Ruben,(2) using radioactive C^{14} isotope as a tracer. The particular mechanism proposed by Brandner and Urey was based on the assumption of the presence of the activated forms of water and hydrogen (or activated hydrogen atom and hydroxyl radical) on the surface with the condition that the total amount of these molecules is constant.

The catalytic water gas reaction on the surface of a heated platinum wire in the region of 1,000°C.(3) is a famous one, and it is also generally known that water vapor and hydrogen are strongly adsorbed on quartz at these high temperatures. Nevertheless, unfortunately, the present author cannot accept their particular mechanism mentioned above for the following reasons:

(1) it seems somewhat doubtful that a considerable amount of water vapor, by which this exchange reaction was pronouncedly accelerated, was inevitably introduced and remained in the vessel,

(2) they have shown no direct evidence for the presence of the condition that the total amount of these activated molecules on the surface is constant.

On the other hand, Norris and Ruben proposed the mechanism of a bimolecular reaction between the two reactant species adsorbed on quartz. But, so far as their experimental results were concerned, it was not confirmed that the reaction is heterogeneous and catalytic.

Therefore, it seemed necessary for the present author to confirm the heterogeneity and the rate law of this exchange reaction.

Experimental

The natural C^{13} isotope, used in these experiments, was made by Prof. T. Titani(4) of Osaka University from the thermal diffusion of methane, and was fixed as silver carbonate. Carbon dioxide enriched in C^{13} was prepared from the thermal decomposition of silver carbonate and purified by several fractionations. Carbon monoxide was prepared from the decomposition of purified formic acid by heated phosphoric acid and purified by the usual method. During these purifications, water vapor was carefully prevented from entering into either of the sample gases. Argon was taken from cylinders, and was purified of oxygen and nitrogen by passage over hot copper turnings and then by calcium-arc discharges.

The reason for employing the C^{13} isotope (but not the O^{18} isotope) in these kinetic measurements has already been pointed out by Brandner and Urey.

A 55 cc. cylindrical quartz vessel (inner dia. 14 mm., length 35 cm.) was used in all runs. In testing for heterogeneity, the reaction vessel was packed with short sections of quartz tubing, whereby the surface-to-volume ratio was increased twofold approximately. The reaction vessel was connected to a glass high vacuum system through a water-cooled capillary graded seal, and closed by a capillary stopcock. Since the volume of the system was minimized by using 1.4 mm. capillary tubing throughout, the dead space between the reaction vessel and the stopcock was very small (about 0.8 cc.) compared with the volume of the reaction vessel, no correction for this was made for the results given in Table 1 and Table 2.

In these experiments the gases were premixed and introduced simultaneously into the hot quartz vessel, previously evacuated to $\approx 10^{-5}$ mm.Hg. and maintained in this vacuum during the period of 8-10 hrs. After the desired time the gases were pumped out and analysed by a mass spectrometer.

The mass spectrometer used in these experiments was of the 90° sector type, and the radius of curvature of the ion path was 13.0 cm. The details of this mass spectrometer were previously reported.(5) Though it seemed convenient to use

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* This investigation was partly reported in the Annual Meeting of Chem. Soc. Japan (April, 1951).

(1) J. D. Brandner and H. C. Urey, *J. Chem. Phys.*, **13**, 351 (1945).

(2) T. H. Norris and S. Ruben, *J. Chem. Phys.*, **18**, 1595 (1950).

(3) C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 806 (1925).

(4) T. Titani and S. Horibe, *J. Chem. Soc. Japan*, **73**, 75 (1952).

(5) T. Hayakawa and T. Kambara, *J. Chem. Ind. Japan*, **54**, 310 (1951).

the same method with Urey and Brandner's, i. e., the direct connection of the reaction vessel to the ionization chamber of the mass spectrometer, the present author unfortunately could not use this method since the present instrument was designed for common use.

The reproducibility of this instrument for isotopic concentrations was ±0.01 (in atomic percentages); therefore, the good reproducibility was obtained in these usual runs. But, since the initial concentrations of $C^{13}O_2$ in these experiments were considerably low, the reproducibility in these several runs at the temperature of 710°C. was considerably poor. Herein, in these special runs, the average value of several measurements was adopted.

Result

The experimental results are summarized in Table 1 and Table 2, where the run numbers indicate the chronological order of the experiments.

Assuming that

(a) there is no isotope effect of C^{13}, and

(b) at equilibrium, the specific concentration of carbon dioxide (the percentage ratio, $C^{13}O_2$ to total CO_2) is equal to that of carbon monoxide,

the following first-order rate law expression(6)~(9) is easily obtained for the present exchange reaction,

$$C^{13}O_2+C^{12}O \rightleftharpoons C^{13}O+C^{12}O_2$$

$$R=\frac{2.303\,p\mathrm{CO}\cdot p\mathrm{CO}_2}{(p\mathrm{CO}+p\mathrm{CO}_2)t}\log\frac{x_0-x_\infty}{x-x_\infty} \qquad (1)$$

where R denotes the exchange rate, and x_0, x, x_∞, each denotes the specific concentration of carbon dioxide (the percentage ratio, $C^{13}O_2$ to total CO_2) at the time of initial, given, and equilibrium respectively.

The exchange rate, R, may also be expressed in the following form*

$$R=C\cdot f(p\mathrm{CO}_2)\cdot\varphi(p\mathrm{CO}) \qquad (2)$$

where C is a constant.

Fig. 1 gives a plot of rate *versus* carbon dioxide pressure at 900°C., at constant carbon monoxide pressure. Fig. 1 shows that the function $f(p\mathrm{CO}_2)$ is simply proportional to carbon dioxide pressure.

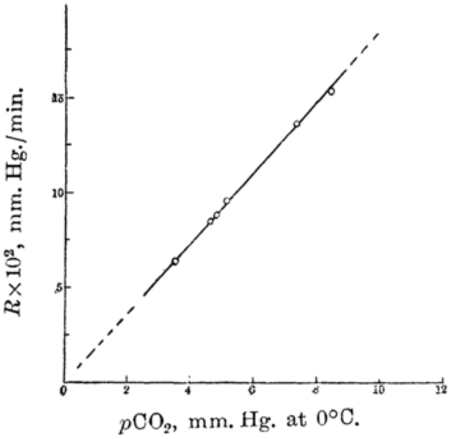

Fig. 1.—Dependence of exchange rate on carbon dioxide pressure at 900°C. $p\mathrm{CO}\approx8.5$ mm. Hg. at 0°C.

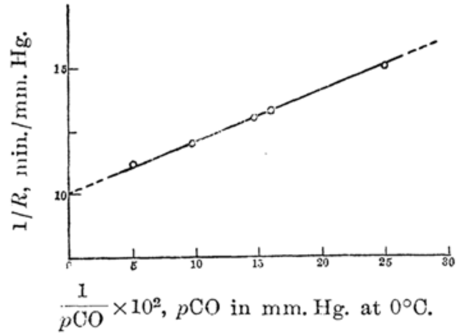

Fig. 2.—Dependence of exchange rate on carbon monoxide pressure at 900°C. $p\mathrm{CO}_2\approx3.9$ mm. Hg. at 0°C. $b=0.51$.

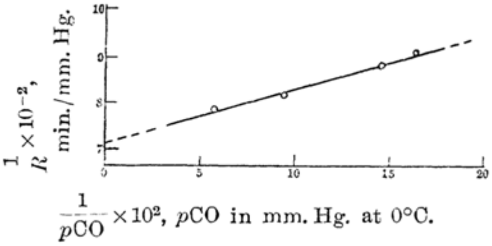

Fig. 3.—Dependence of exchange rate on carbon monoxide pressure at 770°C. $p\mathrm{CO}_2\approx3.5$ mm. Hg. at 0°C. $b=0.62$.

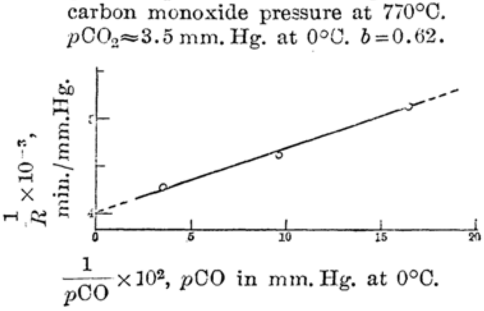

Fig. 4.—Dependence of exchange rate on carbon monoxide pressure at 710°C. $p\mathrm{CO}_2\approx4.8$ mm. Hg. at 0°C. $b=0.74$.

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(6) H. A. C. McKay, *Nature*, **142**, 997 (1938).

(7) R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.*, **68**, 557 (1946).

(8) J. W. Weigl and M. Calvin, *J. Chem. Phys.*, **17**, 210 (1949).

(9) K. S. Pitzer, *J. Chem. Phys.*, **17**, 1341 (1949).

* See, for example: H. A. C. McKay, *Nature*, **142**, 997 (1938).

On the other hand, a log-log plot of rate *versus* carbon monoxide pressure at 900°C., carbon dioxide pressure remaining constant, gives with a poorer approximation to a straight line, a slope of 0.2. So, the present author has adopted the following expression,

$$\varphi(p\mathrm{CO})=C'\frac{p\mathrm{CO}}{1+b\cdot p\mathrm{CO}} \qquad (3)$$

where C' is a constant, and b is a constant depending on the temperatures.

Fig. 2, Fig. 3, and Fig. 4 indicate that this expression (3) is quite satisfactory for the present results. Then, the following rate law is obtained.

$$R=k\frac{p\mathrm{CO}\cdot p\mathrm{CO}_2}{1+b\cdot p\mathrm{CO}} \qquad (4)$$

Table 1

Exchange between CO_2 and CO (no additives).

Run	Time (min.)	Pressures (mm.Hg. at 0°C.)		Sp. concentrations					k,	($k'\times10^2$)
		CO	CO_2	CO_2			CO			
				x_0	x	(x_∞) calcd.	y_0	y		
				Experiments at 710°±2°C.						
32	365	29.4	5.9	3.14	3.11	1.43	1.09	1.10	3.09×10^{-5}	
34	420	23.5	4.7	3.14	3.10	1.43	1.09	1.11	3.63	
35	510	10.3	6.0	3.12	3.08	1.82	1.08	1.09	3.01	
36	720	8.4	4.9	3.12	3.07	1.82	1.08	1.10	2.64	
38	810	6.1	5.9	3.13	3.08	2.10	1.09	1.16	2.96	
				Experiments at 770°±2°C.						
41	54	17.6	3.5	3.14	3.10	1.43	1.09	1.10	2.10×10^{-4}	
43	60	6.2	3.5	3.12	3.08	1.82	1.08	1.12	2.44	
44	60	12.2	7.0	3.12	3.07	1.82	1.08	1.12	2.32	
45	180	9.4	5.4	3.12	2.99	1.82	1.08	1.20	2.70	
46	120	6.2	3.5	3.12	3.04	1.82	1.08	1.14	2.64	
49	30	8.9	4.3	3.15	3.13	1.78	1.09	1.10	2.38	
50	180	6.9	3.4	3.15	3.03	1.78	1.09	1.21	2.55	
				Experiments at 900°±2°C.						
7	120	19.6	3.9	3.14	1.49	1.43	1.09	1.42	1.29×10^{-2}	(2.79)
9	270	9.4	4.0	3.14	1.68	1.68	1.09	1.69	—	
10	30	10.1	4.0	3.14	2.29	1.68	1.09	1.43	1.28	(2.91)
11	60	8.6	3.5	3.14	1.99	1.68	1.09	1.61	1.16	(3.05)
12	75	7.5	3.0	3.14	1.83	1.68	1.09	1.62	1.40	(3.04)
16	30	11.2	6.4	3.12	2.34	1.82	1.08	1.55	1.17	(3.06)
17	60	6.7	3.9	3.12	2.02	1.82	1.08	1.70	1.30	(3.12)
18	60	8.7	5.1	3.12	2.04	1.82	1.08	1.71	1.17	(2.96)
19	120	8.5	4.9	3.12	1.86	1.82	1.08	1.79	1.16	(2.90)
20	180	9.0	5.1	3.12	1.82	1.82	1.08	1.81	—	
21	90	8.4	4.8	3.12	1.90	1.82	1.08	1.77	1.25	(3.15)
23	30	8.7	8.4	3.13	2.46	2.10	1.09	1.67	1.14	(3.50)
24	60	5.7	5.5	3.13	2.28	2.10	1.09	1.93	1.02	(2.88)
26	150	7.2	7.0	3.13	2.10	2.10	1.09	2.11	—	
27	90	4.0	3.9	3.13	2.15	2.10	1.09	2.06	1.31	(3.36)
29	60	8.7	7.4	3.13	2.16	2.03	1.09	1.93	1.06	(3.56)
30	180	6.1	5.2	3.13	2.03	2.03	1.09	2.03	—	
				Experiments at 900°±2°C. (Packed)						
54-P	15	6.7	4.5	3.15	2.48	1.90	1.08	1.53	2.03×10^{-2}	
55-P	30	6.3	4.2	3.15	2.22	1.90	1.08	1.68	1.82	
56-P	60	8.9	6.1	3.15	1.94	1.90	1.08	1.87	2.12	
57-P	45	8.7	5.9	3.15	2.03	1.90	1.08	1.82	1.87	
59-P	120	9.7	6.5	3.15	1.90	1.90	1.08	1.91	—	

Accordingly, the equation (1) becomes

$$\frac{2.303\,p\mathrm{CO}\cdot p\mathrm{CO_2}}{(p\mathrm{CO}+p\mathrm{CO_2})\,t}\log\frac{x_0-x_\infty}{x-x_\infty}=k\frac{p\mathrm{CO}\cdot p\mathrm{CO_2}}{1+b\cdot p\mathrm{CO}} \qquad (5)$$

This equation (5) has been used to calculate the values of k given in Table 1 and Table 2. It is seen that the agreement among all the runs is fairly good.

The average k values (unpacked, non-additives) have been plotted in Fig. 5 as the logarithm of k *versus* $1/T$. The fact that the points give a reasonable approximation to a straight line suggests that there is but one exchange mechanism in this temperature range. The slope of this plot indicates an apparent activation energy of 73 kcal./mol., and this value is in good agreement with the value of 77 kcal./mol. obtained by Norris and Ruben.

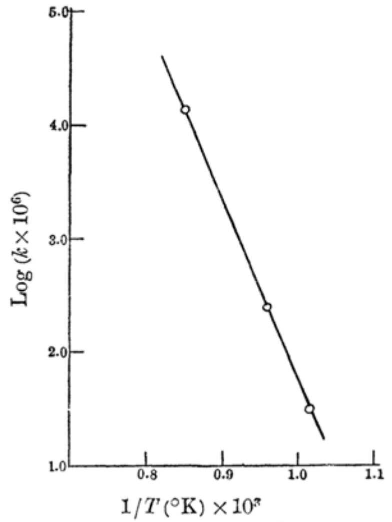

Fig. 5.—Temperature dependence of rate constant.

In order to test for heterogeneity, the reaction vessel was packed with short sections of quartz tubing, thus increasing the surface-to-volume ratio twofold approximately. From the results shown also in Table 1, it is clear that the rate of this exchange reaction is considerably increased by packing, though this increase in the rate is not correctly proportional to the surface-to-volume ratio. And this effect of packing is, as a tendency, similar to the results obtained by Brandner and Urey, but it is inconsistent with the results of Norris and Ruben.

The present results on the effect of water and argon are indicated in Table 2. As seen in Table 2, the addition of argon has no influence (rather slight retardation) on this reaction within the experimental error. On the other hand, the addition of water apparently indicates a pronounced acceleration. But as discussed below, this apparent acceleration caused by adding water is not real.

Discussion

From the facts that the reaction is considerably retarded by carbon monoxide and is

Table 2

The Influence of Argon and Water (at 900°C.)

(1) Argon addition (10 vol. %)

Run	Time (min.)	Pressures (mm.Hg. at 0°C.)			Sp. concentrations					$k\times10^2$
					CO_2			CO		
		CO	CO_2	Ar	x_0	x	(x_∞) cal.	y_0	y	
51	15	11.1	2.0	1.3	3.14	2.62	1.41	1.09	1.18	1.04
52	30	8.2	1.5	1.0	3.14	2.39	1.41	1.09	1.24	1.02
53	60	16.8	3.0	2.0	3.14	1.97	1.41	1.09	1.31	0.90

(2) Water addition ($x_0=3.14$, $y_0=1.09$).

Run	Time (min.)	Initial pressures (mm.Hg. at 0°C.)				x	Composition $(CO_2)/(CO)+(CO_2)$		$\frac{(C^{13}O_2)}{(C^{13}O_2)_0}$
		CO	CO_2	H_2O			initial (t_0),	final (t),	
62	15	8.6	3.5	1.8	(≈15%)	1.99	0.29	0.33	0.72
63	30	10.1	4.0	2.1		1.71	0.28	0.36	0.70
(10)	(30)	(10.1)	(4.0)	(0)		(2.29)			(0.74)
65	45	7.5	3.1	1.5		1.67	0.29	0.36	0.66
(12)	(75)	(7.5)	(3.0)	(0)		(1.83)			(0.58)
67	15	8.4	3.6	1.0	(≈8%)	2.21	0.30	0.34	0.80
68	30	9.8	4.3	1.2		1.98	0.30	0.35	0.73
70	15	8.6	3.5	2.4	(≈20%)	1.68	0.29	0.37	0.68
72	45	7.6	3.2	2.2		1.59	0.30	0.38	0.63

markedly accelerated by packing, it seems reasonable to consider that this exchange reaction is heterogeneous and catalytic, as it was partly suggested by Urey and Brandner. In the experiments of Norris and Ruben on this question of heterogeneity, the surface-to-volume ratio was increased sixfold by packing, but the k values obtained by them indicated almost no effect. Though they considered that their data might indicate a reaction partly homogeneous, it seems rather reasonable for the present author to consider their data indicating much lower catalytic activity of their quartz. This is partly based on the fact that their k values at 900°C. are very small compared with that of the present author's, and is also partly based on the reasons discussed later.

As generally discussed by Morita,(10) the relations expressed in equation (1) and (2) are, in themselves, well explained whenever the rate-determining process of the catalytic exchange reaction is the direct exchange between the two reactant species or the adsorption (or the desorption) of any one of the reactants. But, from the fact that the present results are well satisfied by the rate law expression (4), it seems reasonable for the present author to believe that this exchange reaction is obeyed in any one of the following mechanisms.

Mechanism (1)—

$$C^{13}O_2 \text{ (gas phase)} + C^{12}O \text{ (adsorbed)} \rightleftarrows$$
$$C^{13}O \text{ (adsorbed)} + C^{12}O_2 \text{ (gas phase)}$$
$$R = k \cdot pCO_2 \cdot \varphi(CO)$$

where $\varphi(CO)$ denotes the adsorbed amount of carbon monoxide.

According to this mechanism (1), the reaction is a bimolecular exchange between the strongly adsorbed carbon monoxide molecule and the carbon dioxide molecule in the gas phase. The function $\varphi(CO)$ may be determined from the adsorption state of carbon monoxide, and in the present experiments it must satisfy the form $c' \cdot pCO/1 + b \cdot pCO$.

Therefore, in order to test for this problem, it was necessary to determine the adsorption states of the two reactant species at the temperatures of these experiments, using the same quartz vessel.

The present observations using a constant volume method(11) have been plotted in Fig. 6. Each line in Fig. 6 corresponds to each separated adsorption isotherm at 900°C. Fig. 6 shows that the adsorption of carbon monoxide on this quartz surface is considerably large, especially in comparison with that of carbon dioxide, and the adsorbed amount of each reactant is simply proportional to its pressure approximately.

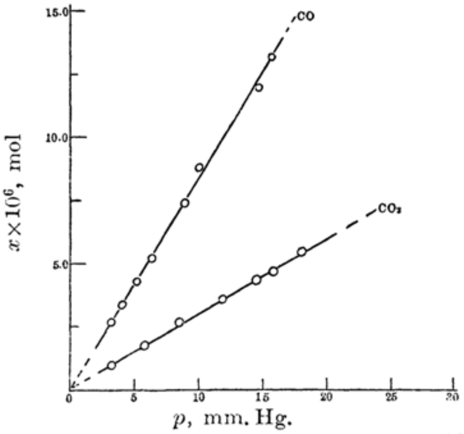

Fig. 6.—Adsorption isotherm on quartz at 900°C.

Then, according to mechanism (1), the present adsorption experiments must result in the rate law

$$R = k \cdot pCO \cdot pCO_2$$

However, unfortunately, thus obtained rate law is inconsistent with the results of this exchange reaction expressed in equation (4).

But, since the present observations in testing for the adsorption of carbon monoxide were obtained for the total surface of the reaction vessel and in this condition the adsorption of carbon monoxide was stronger than that of carbon dioxide at this high temperature, it seems also probable that the adsorption of carbon monoxide on the active surfaces for this reaction may be rather strong and may obey the usual Langmuir's isotherm.

$$\varphi(CO) = C' \cdot pCO/1 + b \cdot pCO$$

Therefore, the present results of this exchange reaction are well explained by mechanism (1).

On the other hand, since it is probable to think of the present exchange reaction as an oxidation of carbon monoxide by carbon dioxide, many studies(12)~(15) of the carbon

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(10) N. Morita, This Bulletin, **15**, 166 (1940); *J. Chem. Soc. Japan*, **44**, 62 (1941).

(11) See, for example: A. F. Benton and T. A. White, *J. Am. Chem. Soc.*, **52**, 2325 (1930).; W. J. C. Orr, *Proc. Roy, Soc.*, **A173**, 349 (1939).

(12) M. Bodenstein and F. Ohlmer, *Zeit. Phys. Chem.*, **53**, 166 (1905).

(13) A. F. Benton and T. L. Williams, *J. Phys. Chem.*, **30**, 1487 (1923).

(14) F. Handman, H. W. Thompson and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A137**, 87 (1932).

(15) Y. Kondo and O. Toyama, *Rev. Phys. Chem, Japan*, **13**, 166 (1939).

monoxide-oxygen reaction in quartz must show certain similarities to the present one.

These studies have shown that this dry and non-explosive oxidation at the temperatures lower than 800°C. is heterogeneous and that strongly adsorbed carbon monoxide and rather weakly adsorbed oxygen interact each other.

Although the results of these studies mentioned above are inconsistent with mechanism (1), we must consider the difference between oxygen and carbon dioxide in the adsorptive properties.

Mechanism (2)—

$$C^{12}O\ (\text{adsorbed}) + C^{13}O_2\ (\text{adsorbed}) \rightleftarrows C^{12}O_2\ (\text{adsorbed}) + C^{13}O\ (\text{adsorbed})$$

$$R = C \cdot f(pCO_2) \cdot \varphi(pCO)$$

According to the present observations, the adsorptions of carbon monoxide and carbon dioxide were both rather weak and the adsorbed amount of each reactant in each separated adsorption isotherm at 900°C. was simply proportional to its pressure. However, since these results were obtained for the total surface of the quartz vessel, when each reactant is adsorbed on each different surface (without mutual displacement) and the adsorption of carbon monoxide on the active surfaces for this reaction is moderate the rate of this exchange reaction follows⁽¹⁶⁾

$$R = k \cdot \frac{pCO}{1 + b \cdot pCO} \cdot pCO_2$$

This rate law coincides well with expression (4).

Moreover, since the catalytic activities of various kinds of quartz vary considerably when the adsorptions of carbon monoxide and carbon dioxide on the different active surfaces are both moderate, the rate of this exchange reaction seems to follow⁽¹⁷⁾

$$R = k \cdot \frac{pCO}{1 + b \cdot pCO} \cdot \frac{pCO_2}{1 + b' \cdot pCO_2} \approx k \cdot pCO^m \cdot pCO_2^{\,n}$$

The rate law thus obtained is in good agreement with the results of Norris and Ruben ($m \approx 0.7$, $n \approx 0.85$).

On the other hand, one may derive the similar rate law when two reactant species are both moderately adsorbed on the same surface and $1 \gg (b \cdot pCO)^2$, $(b' \cdot pCO_2)^2$,

$$R = k \cdot \frac{pCO \cdot pCO_2}{(1 + b \cdot pCO + b' \cdot pCO_2)^2} \approx k \cdot pCO^m \cdot pCO_2^{\,n}$$

However, unfortunately, the present results of this exchange reaction are unexplained by the adsorptions of two reactant species on the same surface. And from the fact that the value of the apparent activation energy of this exchange reaction obtained by the present author is in good agreement with that of Norris and Ruben, it seems probable that the reaction, both in the present author's and in that of Norris and Ruben, obeys a similar mechanism.

From these reasons mentioned above, though the present results are well explained by both mechanisms (1) and (2), the latter seems more probable to the present author.

In both mechanism (1) and (2), it is also necessary to ascertain the influence of the side reaction on the quartz surface.

$$2CO \rightleftarrows CO_2 + C$$

This reaction on a nickel catalyst was investigated in detail by Rhi.⁽¹⁸⁾

The present results in testing for this reaction, using the same quartz vessel, are shown in Table 3. Table 3 shows that this reaction slightly occurs at the temperatures of these experiments. However, as it was also suggested by Brandner and Urey, since the pressure of the gas mixture and the percentage of carbon monoxide was not sufficiently high in any present exchange experiment to cause deposition of massive carbon on the walls of the quartz vessel, the influence of this side reaction on the present exchange reaction appears to be very small.

Table 3

The Decomposition of Carbon Monoxide (at 900°C.).

Initial Pressure pCO (mm.Hg. at 0°C.)	Time t (min.)	CO_2, formed (vol. %)
10.9	60	0.7
10.7	180	1.0
21.2	60	1.2
21.2	120	1.5
30.6	30	1.1
30.6	63	1.9
30.9	120	2.4

The mechanism suggested by Brandner and Urey is an excited water gas reaction on the walls of the quartz vessel.

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(16) See, for example: G. M. Schwab, *Zeit. Elektrochem.*, **35**, 573 (1929). ($2CO + O_2 = 2CO_2$, on SiO_2).

(17) See, for example: C. R. Prichard and C. N. Hinshelwood, *J. Chem. Soc.*, **127**, 1546 (1925).

(18) T. Rhi, *Rev. Phys. Chem. Japan*, **8**, 89 (1934); **10**, 200 (1936).

$$H_2 = H_2^*$$
$$C^{13}O_2 + H_2^* \rightleftarrows C^{13}O + H_2O^*$$
$$H_2O^* \rightarrow H_2O$$
$$(H_2^*) + (H_2O^*) = \text{constant}$$

They considered that their mechanism might be supported, though it was not entirely free of difficulties, by the fact that the exchange rate was markedly accelerated by adding hydrogen or water vapor.

As has been mentioned, the study of the catalytic water gas reaction on the surface of a heated platinum wire is a famous one.

And it seems also probable that hydrogen and water vapor are strongly adsorbed on quartz at the temperatures of these experiments and, then, they cause a marked acceleration of this exchange reaction.

Indeed, as seen in Table 2, since the values of x (percentage ratio, $C^{13}O_2$ to total CO_2) are markedly decreased in these experiments, the addition of water apparently causes a pronounced acceleration of this exchange reaction. However, it must be noticed that in each run of adding water the final concentration of carbon dioxide is also considerably increased and, then, this acceleration is only apparent and not true. The true acceleration caused by adding water must be much smaller than this, and may be measured by $(C^{13}O_2)/(C^{13}O_2)_0$ in Table 2, where $(C^{13}O_2)_0$ and $(C^{13}O_2)$ each denotes the concentration of $C^{13}O_2$ at the initial and given time respectively. Accordingly, the present results shown in Table 2 indicate that the true acceleration is somewhat increased with the water contents. This would seem inconsistent with Brandner and Urey's important assumption in their mechanism, because their mechanism is based on the assumption that the surface is completely covered by these molecules of H_2^* and H_2O^* and that the total amount of these molecules is constant. And it seems also very difficult for the present author to suppose that in each exchange experiment of no additives the considerable amount of water vapor remained in the reaction vessel. Moreover, unfortunately, Brandner and Urey's mechanism fails to explain the fact of the exchange rate in the present experiments obeying expression (4).

The present author calculated the rate constant, k', on the basis of Brandner and Urey's rate law and mechanism. Although each value of k' (at 900°C.) given in Table 1 apparently indicates rather good agreement, this may be attributed to the fact that the value of $1 + b\cdot pCO/pCO + pCO_2$ in the present experiments at 900°C. is not very different from the others.

From these reasons it seems inevitable for the present author to consider that the mechanism suggested by Brandner and Urey (a excited water-gas reaction) is, in itself, a different reaction from the present exchange reaction, though it contains many interesting suggestions.

Conclusions

It has been concluded that this exchange reaction is heterogeneous and catalytic.

The rate of this reaction has the form of a product of adsorption isotherms. The probable mechanism—and then the probable rate determining process—of this exchange reaction seems to be a bimolecular exchange (oxidation) reaction between the two reactant species adsorbed on quartz. Although a similar mechanism was already suggested by Norris and Ruben, they had failed to confirm the heterogeneity of this reaction.

The present results are somewhat different from those of Norris and Ruben. In the present experiments, it seems probable to consider that each reactant is adsorbed on each different surface and the adsorption of carbon monoxide on the active surfaces for this exchange reaction is moderate, but carbon dioxide is rather weakly adsorbed.

The results obtained by Norris and Ruben suggest to us that the adsorption of the two reactant species in their experiments are both moderate and not very different.

It is supposed that the observed difference between the results of Norris and Ruben and that of the present author may be attributed to the difference in the catalytic activity of quartz.

The present exchange reaction is somewhat accelerated by adding water. Probably it may depend on the occurrence of the water gas reaction,

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

Although Brandner and Urey proposed this mechanism (an excited water gas reaction) for the present exchange reaction, their mechanism does not satisfy the present results of this exchange reaction.

Therefore, so far as the present experiments are concerned, the present author considers that the reaction mechanism is fundamentally different in the presence and in the absence of water vapor or hydrogen.

The author wishes to express his grateful thanks to Professor T. Titani of Osaka University who kindly offered his precious sample of C^{13} isotope and also many helpful suggestions on this problem, and to Professor O. Toyama of Naniwa University for his kind discussions.

The author is also greatly indebted to Dr. T. Kambara of the Central Laboratory of Hitachi Factory for using his mass spectrometer.

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