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ON THE MECHANISM OF WATER GAS SHIFT REACTION

Part II. Determination of Stoichiometric Number of Rate-determining Step by means of ^{14}C as Tracer.

By

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Abstract

The stoichiometric number ν_r of rate-determining step of catalyzed water gas shift reaction in the presence of iron oxide catalyst has been determined at temperatures 385, 386 and 405°C and total pressure of 80 mmHg by means of radioactive carbon as tracer. The overall reaction rate and the specific β -ray count of radioactive carbon in carbon dioxide in course of approaching the equilibrium were concurrently followed in each run of experiment and ν_r was determined from the results. The ν_r thus obtained was definitely unity in order of magnitude. The present results is in agreement with the conclusion arrived at previously by ENONOTO and UGAJIN⁴⁾ in equilibrium.

Incorporating the present result with the previous one⁵⁾ that ν_r was found unity by means of deuterium as tracer according to the same equation, it is concluded that the possible mechanism among the proposed ones is that advanced by KAGIYA, SENO and FUKUI⁶⁾ as well as LANGMUIR-HINSHLEWOOD mechanism and RIDEAL-ELEY mechanism as stated in part I⁵⁾, but conflicts with those of TEMKIN⁹⁾ and TAMARU¹⁰⁾. The latter reasoning implies a method of discerning the pertinence of a sequence of steps, usually attributed to an overall reaction just by physical intuition, on the basis of the knowledge of the set of ν_r -values by order of magnitude as obtained by means of different tracers, *e.g.*, radioactive carbon and deuterium in this case.

I. Introduction

It has generally been accepted that the observation of stoichiometric number provided a powerful method of determining the mechanism of chemical reaction.

The present paper is devoted to establishing the mechanism of the catalyzed water gas shift reaction



in the presence of iron oxide catalyst by determining the stoichiometric number

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ν_r of the rate-determining step by means of radioactive carbon as tracer. Assuming that reaction (1) proceeds through the sequence of steps,



and



we see that the stoichiometric number of every step above is unity with reference to stoichiometric equation (1).

The stoichiometric number is now determined, as in the previous work, by an equation¹⁾

$$\nu_r = -\Delta G/RT \ln (V_+/V_-) \quad (3)$$

by measuring the affinity $-\Delta G$, forward unidirectional rate V_+ and the backward one V_- of the overall reaction simultaneously in course of the progress of overall reaction toward equilibrium.

The V_+ or V_- is determined by means of isotope tracer on the premise that the observed isotopic transfer takes place solely through the rate-determining step. If otherwise, *i.e.*, the transfer occurs through other constituent step s' than the rate-determining step r , the ν_r -value as determined on the basis of the above premise equals the ratio of the unidirectional forward rate of step s' to that of r as shown by FRUMKIN²⁾ with reference to a particular example and generally by MATSUDA and HORIUTI³⁾. The ratio of the unidirectional forward rate of s' to that of r will be denoted conventionally by ∞ in what follows. For instance, if one uses radioactive carbon as tracer $\nu_r=1$ only in the case where the second step of the above sequence determines the rate but ∞ otherwise.

The ν_r of reaction (1) has previously been determined by ENOMOTO and UGAJIN⁴⁾ to be unity by means of radioactive carbon as tracer in equilibrium. The ν_r determined by deuterium as tracer must now be ∞ , insofar as the sequence of steps (2) is operative. However, the ν_r thus obtained by present authors in terms of simultaneous measurements mentioned above was definitely unity in order of magnitude, even if the isotopic effect is taken into account. Incorporating this result with ENOMOTO and UGAJIN's result, it was concluded that a possible mechanism is that of LANGMUIR-HINSHAW mechanism or RIDEAL-ELEY mechanism, insofar as there exists a rate-determining step⁵⁾. However, ENOMOTO and UGAJIN obtained only two values of ν_r by a procedure of measuring the overall and unidirectional forward rate severally with

On the Mechanism of Water Gas Shift Reaction II

different samples of gas, which is liable to objections.

It is tried in the present work to determine ν_r by simultaneous measurements mentioned above by means of radioactive carbon as tracer in order to avoid the above disadvantage. It has been found⁶⁾, however, that carbon atom was exchanged directly between carbon monoxide and carbon dioxide in the absence of water vapor and hydrogen, which was taken into consideration in evaluation of ν_r of reaction (1).

The ν_r -value of reaction (1) has thus been found unity in order of magnitude at 80 mmHg total pressure in the temperature range from 385°C to 405°C. Principles of the determination of ν_r , experimental procedures and results are described in what follows.

II. Principles of ν_r -Evaluation

The $-ΔG$ in Eq. (3) is expressed in terms of partial pressure P^{CO} , P^{H_2O} , P^{CO_2} and P^{H_2} respectively of carbon monoxide, water vapor, carbon dioxide and hydrogen, and the equilibrium constant K_p , assuming the ideal gas law, as¹⁾

$$-ΔG = RT \ln (P^{CO} P^{H_2O} K_p / P^{CO_2} P^{H_2}). \quad (4)$$

The overall reaction rate V of reaction (1) is expressed as

$$V = V_+ - V_- = dn^{CO_2}/dt, \quad (5)$$

where n^{CO_2} is the number of moles of carbon dioxide containing radioactive carbon in the reaction system. The V_- in Eq. (3) is now connected as follows with the transfer rate of radioactive carbon from carbon dioxide to carbon monoxide, provided that the isotopic difference of rates is ignorable and radioactive carbon atoms are transferred in either direction only through the rate-determining step of reaction (1); the rate of transfer radioactive carbon from carbon dioxide to carbon monoxide is then expressed either as $-d(n^{CO_2} Z^{CO_2})/dt$ or as $(Z^{CO_2} V_- - Z^{CO} V_+)$, hence

$$-d(n^{CO_2} Z^{CO_2})/dt = (Z^{CO_2} V_- - Z^{CO} V_+), \quad (6)$$

where Z^{CO} and Z^{CO_2} are the atomic fraction of radioactive carbon in carbon monoxide and in carbon dioxide respectively. Since Z^{CO} and Z^{CO_2} are proportional to the specific β -ray counts C^{CO} and C^{CO_2} of radioactive carbon in carbon monoxide and in carbon dioxide, we have from Eq. (6)

$$-d(n^{CO_2} C^{CO_2})/dt = (C^{CO_2} V_- - C^{CO} V_+). \quad (7)$$

However, the exchange reaction of radioactive carbon occurred directly between carbon monoxide and carbon dioxide in the absence of water vapor

and hydrogen as mentioned above. The above direct exchange between carbon monoxide and carbon dioxide may proceed simultaneously with that through the rate-determining step of the water gas shift reaction. Assuming that the direct exchange occurs concurrently at the same rate as in the absence of water vapor and hydrogen, the rate of transfer of radioactive carbon from carbon dioxide to carbon monoxide should be expressed either as $-d(n^{\text{CO}_2}C^{\text{CO}_2})/dt$ or as $(C^{\text{CO}_2}V_- - C^{\text{CO}}V_+) + k_{\text{ex}}(C^{\text{CO}_2} - C^{\text{CO}})$, hence

$$-d(n^{\text{CO}_2}C^{\text{CO}_2})/dt = (C^{\text{CO}_2}V_- - C^{\text{CO}}V_+) + k_{\text{ex}}(C^{\text{CO}_2} - C^{\text{CO}}), \quad (8)$$

where k_{ex} is the overall rate of unidirectional carbon transfer between carbon monoxide and carbon dioxide. The initial rate of the direct exchange reaction is written, on the other hand, as

$$-n_0^{\text{CO}_2}dC^{\text{CO}_2}/dt = k_{\text{ex}}C_0^{\text{CO}_2} \quad (9. I)$$

or

$$k_{\text{ex}} = -n_0^{\text{CO}_2}(d \ln C^{\text{CO}_2}/dt)_{0, \text{ex}}, \quad (9. II)$$

where $(d \ln C^{\text{CO}_2}/dt)_{0, \text{ex}}$ on the right side of Eq. (9. II) is the value of $(d \ln C^{\text{CO}_2}/dt)$ at $t=0$ of the direct exchange reaction and $n_0^{\text{CO}_2}$ is the number of moles of carbon dioxide at the direct exchange. Combining (5), (8) and (9. II), we have

$$\frac{V_+}{V_-} = \frac{1}{1 - \frac{(C^{\text{CO}} - C^{\text{CO}_2})(d \ln P^{\text{CO}_2}/dt)}{(dC^{\text{CO}_2}/dt) - (P_0^{\text{CO}_2}/P^{\text{CO}_2})(d \ln C^{\text{CO}_2}/dt)_{0, \text{ex}}(C^{\text{CO}_2} - C^{\text{CO}})}}, \quad (10)$$

where $P_0^{\text{CO}_2}$ is the partial pressure of carbon dioxide corresponding to $n_0^{\text{CO}_2}$.

Substituting $-dG$ and V_+/V_- respectively from (4) and (10) into (3), we have

$$\nu_r = \frac{\log \{P^{\text{CO}_2}P^{\text{H}}/P^{\text{CO}}P^{\text{H}_2\text{O}}K_p\}}{\log \left[1 - \frac{(C^{\text{CO}} - C^{\text{CO}_2})(d \ln P^{\text{CO}_2}/dt)}{(dC^{\text{CO}_2}/dt) - (P_0^{\text{CO}_2}/P^{\text{CO}_2})(d \ln C^{\text{CO}_2}/dt)_{0, \text{ex}}(C^{\text{CO}_2} - C^{\text{CO}})} \right]}. \quad (11)$$

The ν_r of reaction (1) is now determined according to Eq. (11) by observing the quantities P^{CO} , etc. on its right side simultaneously in course of the progress of reaction (1) with reference to the value of K_p . However, it should be noted that Eq. (11) is exactly applicable only at initial stage of water gas shift reaction, since k_{ex} , which may depend on P^{CO} and P^{CO_2} , is determined at the initial values P_0^{CO} and $P_0^{\text{CO}_2}$ of P^{CO} and P^{CO_2} of the water gas shift reaction. On this ground, ν_r -values are corrected for the direct exchange only for the initial stage of water gas shift reaction.

On the Mechanism of Water Gas Shift Reaction II

III. Experimental

Materials; Carbon monoxide prepared by dehydration of formic acid and purified by passing it through liquid nitrogen trap. Barium carbonate containing radioactive carbon of 2 mc. from ORK RIDGE NATIONAL LABORATORY, England was diluted by 5.0 gr. of "Guaranteed Reagents" of barium carbonate, Koso Chemical Co. Ltd. The mixture was decomposed by perchloric acid to evolve carbon dioxide. Carbon dioxide containing radioactive carbon thus obtained was purified by several times fractional vacuum distillation. Hydrogen prepared by electrolysis of water was passed over Cu-wire kept at 350°C, silica gel, liquid nitrogen trap and finally a palladium thimble kept at 390°C. Distilled water was used without further purification.

Catalyst; Commercial iron oxide catalyst was kindly presented by MITSUBISHI KASEI Co. Ltd. The amount of catalyst used was 1.0 gr. in the state of Fe_2O_3 .

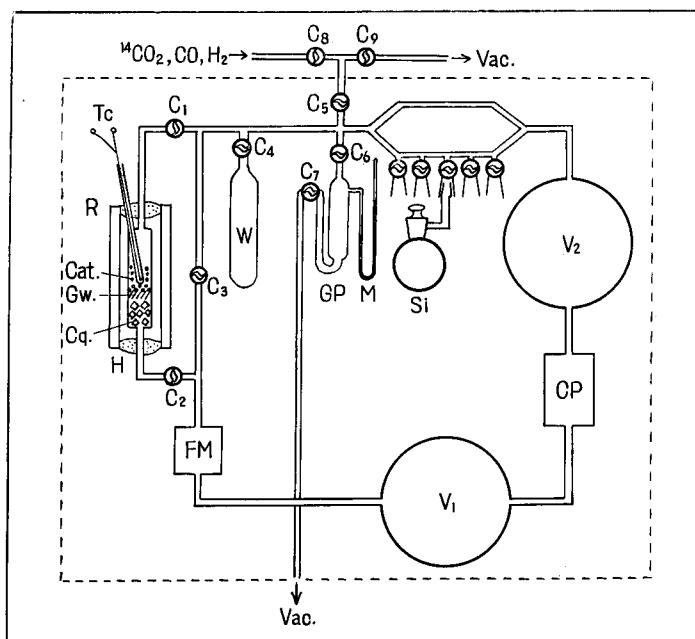


Fig. 1. Circulating system.

R: Reactor	FM: Flow meter
H: Electric furnace	CP: Circulating pump
$C_1 \sim C_9$: Stopcocks	V_1, V_2 : Glass bulb
W: Reservoir of water	Tc: Thermocouple
GP: Gas pipette	Cat: Catalyst
M: Manometer	Gw: Glass wool
Si's: Sampling tube	Cq: Inert material (quartz)

before being reduced to Fe_3O_4 in the working state, particle size being 8–10 mesh. Before starting the measurements, the catalyst was treated with equimolar mixture of carbon dioxide and hydrogen of 80 mmHg total pressure for a few ten hours at 520°C and several times with equimolar mixture of carbon monoxide and water vapor of 80 mmHg total pressure for about 20 hours at the temperature of experiment. The catalyst thus treated decayed further although more slowly, not completely attaining a stable activity.

Apparatus; The apparatus used for the reaction is the same as that in part I⁹), except for the gas pipette GP changed as shown in Fig. 1.

Fig. 2 shows the apparatus for separation of carbon dioxide from other components in the sampled gas. Si is a sampling tube, T_1 liquid nitrogen trap, T_2 glass vessel and B_1 or B_2 constriction for sealing.

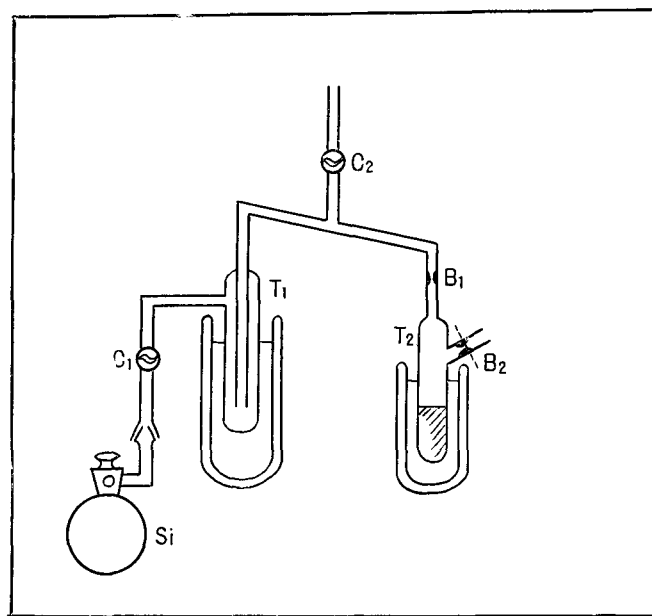


Fig. 2. Apparatus for CO_2 -separation.

- Si: Sampling tube
- T_1 : Liquid nitrogen trap
- T_2 : Glass vessel
- C_1, C_2 : Stopcocks
- B_1, B_2 : Constrictions

Experimental procedures; Experimental procedures of water gas shift reaction were the same as described in part I⁹). Reacted gas was sampled into Si's successively along with the progress of the water gas shift reaction toward

On the Mechanism of Water Gas Shift Reaction II

equilibrium. The carbon dioxide and water vapor were condensed from the sampled gas, the former converted into barium carbonate, and its specific β -ray count measured by Scintillation Counter No. 57071 supplied from the Scientific Research Institute, Tokyo. The condensed carbon dioxide was converted into barium carbonate as follows. Twenty ml. of barium hydroxide solution was preliminarily introduced into T_2 through B_2 in an atmosphere of oxygen, B_2 sealed off, T_1 connected to the sampling tube Si through the joint as shown in Fig. 2, immersed in liquid nitrogen trap, C_1 and C_2 opened, evacuated to 10^{-5} mmHg, the tap of sampling tube opened to condense carbon dioxide and water vapor in T_1 , C_1 and C_2 closed and the bath around T_1 removed to transfer the condensation in T_1 into T_2 . B_1 was now sealed off and T_2 was kept at room temperature for about 24 hours to allow barium hydroxide to absorb the separated carbon dioxide. Barium carbonate thus prepared was filtrated, flushed, dried at 100°C for about 3 hours, weighed and its specific β -ray count C^{CO_2} was measured.

Specific β -ray count C^{CO} of radioactive carbon in carbon monoxide was calculated from P^{CO} , P^{CO_2} and C^{CO_2} as

$$C^{\text{CO}} = (P_0^{\text{CO}_2} C_0^{\text{CO}_2} - P^{\text{CO}_2} C^{\text{CO}_2}) / P^{\text{CO}}, \quad (12)$$

where $P_0^{\text{CO}_2}$ and $C_0^{\text{CO}_2}$ denote initial partial pressure of carbon dioxide and initial specific β -ray count of radioactive carbon in carbon dioxide, P^{CO_2} the initial pressure of carbon dioxide plus the decrease ($P_0^{\text{H}_2\text{O}} - P^{\text{H}_2\text{O}}$) of partial pressure of water vapor determined as described in the previous paper⁵⁾, and P^{CO} the initial partial pressure of carbon monoxide minus the decrease ($P_0^{\text{H}_2\text{O}} - P^{\text{H}_2\text{O}}$).

The exchange reaction



as catalyzed by the same sample of iron oxide was observed in the absence of water vapor and hydrogen as follows.

Carbon monoxide and carbon dioxide, respectively of about 20 mmHg partial pressure, were admitted into the circulating system except the reactor R and mixed by circulating it for an hour through the bypass of the reactor. Exchange reaction was started by switching circuit to the catalyst bed and followed by measuring the P^{CO_2} and the specific β -ray count of sample taken from time to time.

The P^{CO_2} was measured by sampling the gas mixture into the gas pipette, carbon dioxide condensed, carbon monoxide evacuated and carbon dioxide condensation evaporated to measure P^{CO_2} . The gas mixture was on the other

Yoshihisa KANEKO and Syoichi OKI

hand sampled into sampling tube, carbon dioxide was condensed and converted into barium carbonate to measure C^{CO_2} similarly to the case of water gas shift reaction.

TABLE 1. Run 1, 405°C.

time of reaction hr.	$P_{\text{H}_2\text{O}}$ mmHg	P_{CO} mmHg	P_{H_2} mmHg	P_{CO_2} mmHg	C^{CO_2} c.p.mmg ⁻¹	$d \ln P^{\text{CO}_2}/dt$	dC^{CO_2}/dt	ν_r
0	20.7	2.05	18.5	17.3	44.1			
0.25	17.9	17.7	21.3	20.1	28.9	0.00430	0.210	1.42
0.58	16.7	16.5	22.5	21.3	30.7	0.00194	0.065 ₉	1.45
1.58	14.7	14.5	24.5	23.3	27.9			
3.25	13.2	13.0	26.0	24.8	23.0			
5.0	10.4	10.2	28.8	27.6	21.0			
7.0	10.7	10.5	28.5	27.3				
9.0	9.4	9.2	29.8	28.6				
12.0	8.9	8.7	30.3	29.1				
15.0	8.8	8.6	30.4	29.2				
18.0	8.7	8.5	30.5	29.3				
21.0	8.7	8.5	30.5	29.3				

TABLE 2. Run 2, 385°C.

time of reaction hr.	$P_{\text{H}_2\text{O}}$ mmHg	P_{CO} mmHg	P_{H_2} mmHg	P_{CO_2} mmHg	C^{CO_2} c.p.mmg ⁻¹	$d \ln P^{\text{CO}_2}/dt$	dC^{CO_2}/dt	ν_r
0	20.7	23.2	23.2	20.6	45.2			
0.5	16.3	18.8	27.6	25.0	37.3	0.113	6.50	0.96
1.5	14.1	16.0	29.8	27.2	34.1	0.0553	2.58	1.05
3.5	12.1	14.6	31.8	29.2	29.8			
6.5	9.6	12.1	34.3	31.7	26.0			
10.5	8.0	10.5	35.9	33.3				
13.0	7.6	10.1	36.3	33.7				
17.0	7.4	9.9	36.5	33.9				
20.0								
21.17	8.0	10.5	35.9	33.3				
22.0	7.7	10.2	36.2	33.6				
29.0	7.6	10.1	36.3	33.7				

On the Mechanism of Water Gas Shift Reaction II

TABLE 3. Run 3, 405°C.

time of reaction hr.	P_{H_2O} mmHg	P_{CO} mmHg	P_{H_2} mmHg	P_{CO_2} mmHg	C^{CO_2} c.p.mmHg ⁻¹	$d \ln P/CO_2/dt$	dC^{CO_2}/dt	ν_r
0	21.4	20.6	18.7	20.7	47.5			
0.5	15.7	15.4	23.9	25.9	37.3	0.140	8.50	0.99
1.25	13.8	13.5	25.8	27.8	32.4	0.0691	3.38	0.95
2.75	11.6	11.3	28.0	30.0	29.7			
4.75	9.9	9.6	29.7	31.7	26.7			
6.75	8.1	7.8	31.5	33.5				
15.0	8.5	8.2	31.1	33.1				
18.0	8.5	8.2	31.1	33.1				
19.0	8.5	8.2	31.1	33.1				

TABLE 4. Run 4, 386°C.

time of reaction hr.	P_{H_2O} mmHg	P_{CO} mmHg	P_{H_2} mmHg	P_{CO_2} mmHg	C^{CO_2} c.p.mmHg ⁻¹	$d \ln P^{CO_2}/dt$	dC^{CO_2}/dt	ν_r
0	20.1	20.9	20.3	20.7	47.6			
0.5	16.7	17.5	23.7	24.1	38.3	0.118	65.0	1.17
1.5	15.0	15.8	25.4	25.8	34.8	0.0583	2.80	0.95
3.5	12.5	13.3	27.9	28.3	31.0			
6.5	11.1	11.9	29.3	28.7	28.6			
10.5	8.6	9.4	31.8	32.2				
14.0	8.5	9.3	31.9	32.3				
17.0	8.0	8.8	32.4	32.8				
20.0	7.8	8.6	32.6	33.0				
25.5	7.8	8.6	32.6	33.0				
27.5	7.8	8.6	32.6	33.0				

IV. Results

The results obtained are summarized in Table 1 to 4. Fig. 3 to 6 shows the plots of P^{H_2O} and C^{CO_2} against time of reaction respectively. The equilibrium constant $K_p = P_e^{CO_2} P_e^{H_2} / P_e^{CO} P_e^{H_2O}$ was determined from the curves, where the equilibrium values $P_e^{CO_2}$ etc. are calculated as $P_e^{CO} = P_0^{CO} + (P_e^{H_2O} - P_0^{H_2O})$, $P_e^{CO_2} = P_0^{CO_2} + (P_0^{H_2O} - P_e^{H_2O})$ and $P_e^{H_2} = P_0^{H_2} + (P_0^{H_2O} - P_e^{H_2O})$, from the final constant value $P_e^{H_2O}$ of P^{H_2O} as read from the curves.

Yoshihisa KANEKO and Syoichi OKI

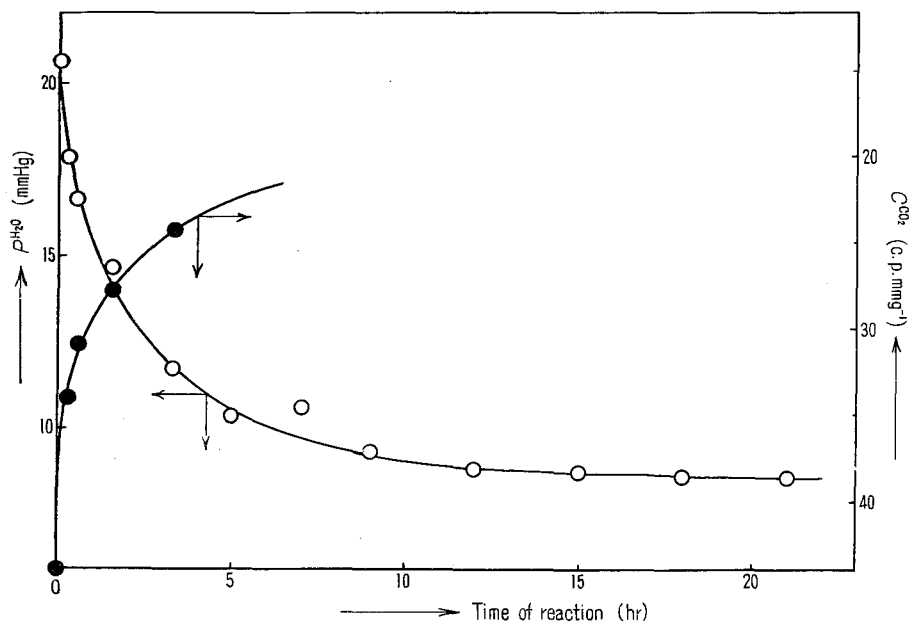


Fig. 3. Partial pressure of water and specific β -ray count vs. time of reaction, run 1.

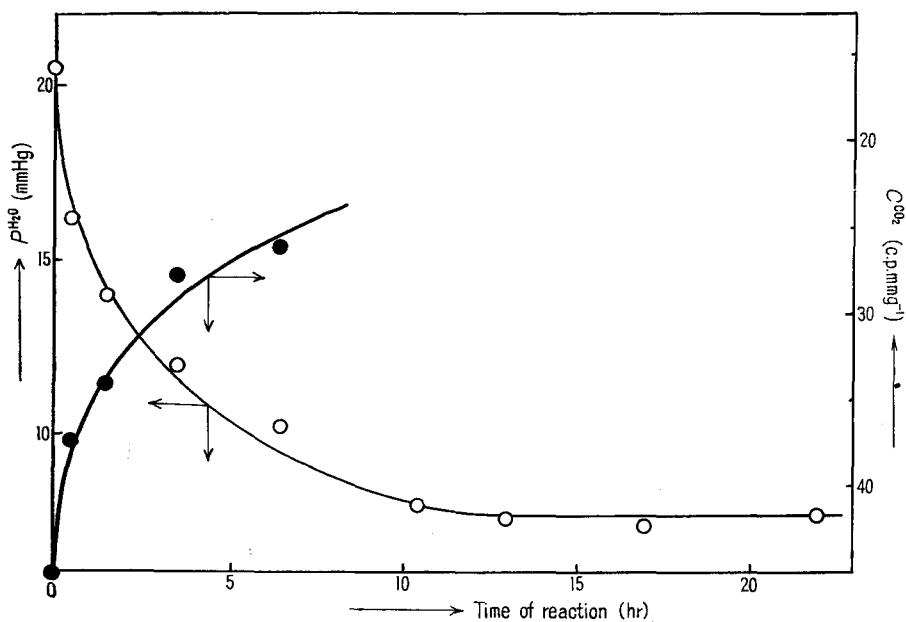


Fig. 4. Partial pressure of water and specific β -ray count vs. time of reaction, run 2.

On the Mechanism of Water Gas Shift Reaction II

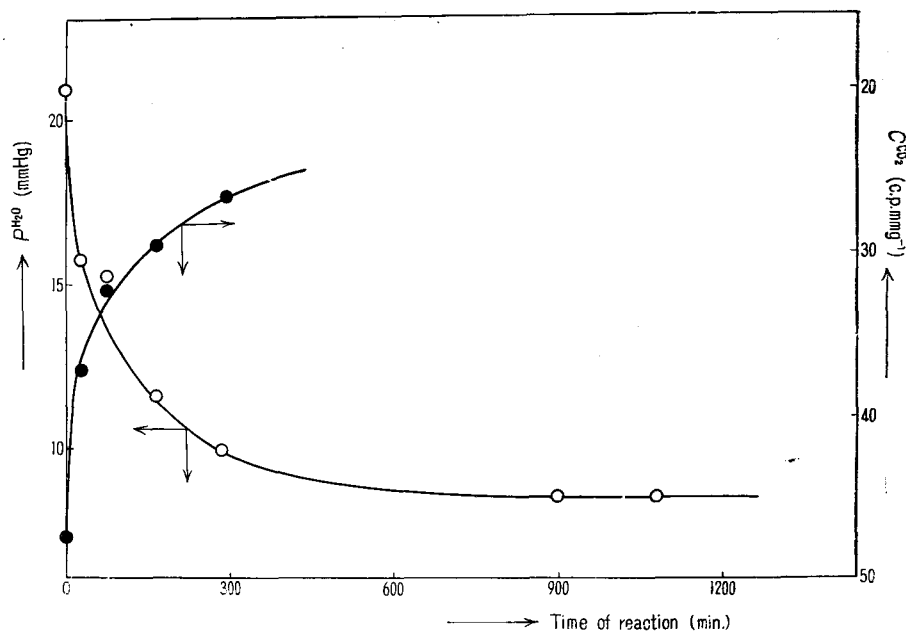


Fig. 5. Partial pressure of water and specific β -ray count vs. time of reaction, run 3.

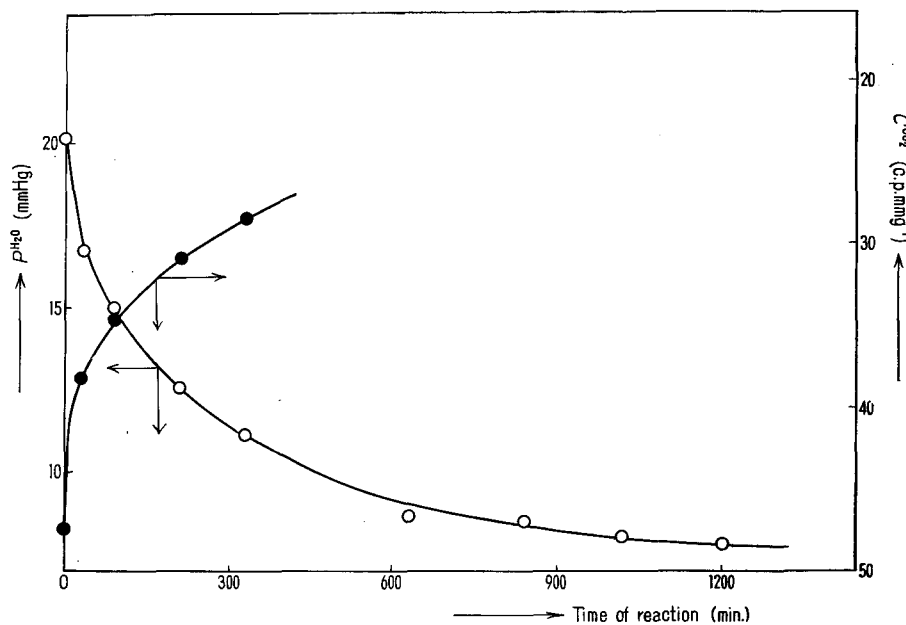


Fig. 6. Partial pressure of water and specific β -ray count vs. time of reaction, run 4.

Fig. 7 shows the plot of $\log C^{\text{CO}_2}$ of the direct exchange reaction in the absence of water vapor and hydrogen against time of reaction. In Fig. 7, \bullet or \circ shows the value at 385°C or 405°C respectively, from which $(d \ln C^{\text{CO}_2}/dt)_{0,\text{ex}}$ at the respective temperature in Eq. (11) was evaluated. No change was found in the ratio of the partial pressure of carbon dioxide to the total pressure, which was reduced stepwise by repeated sampling by 10–20 percent in total.

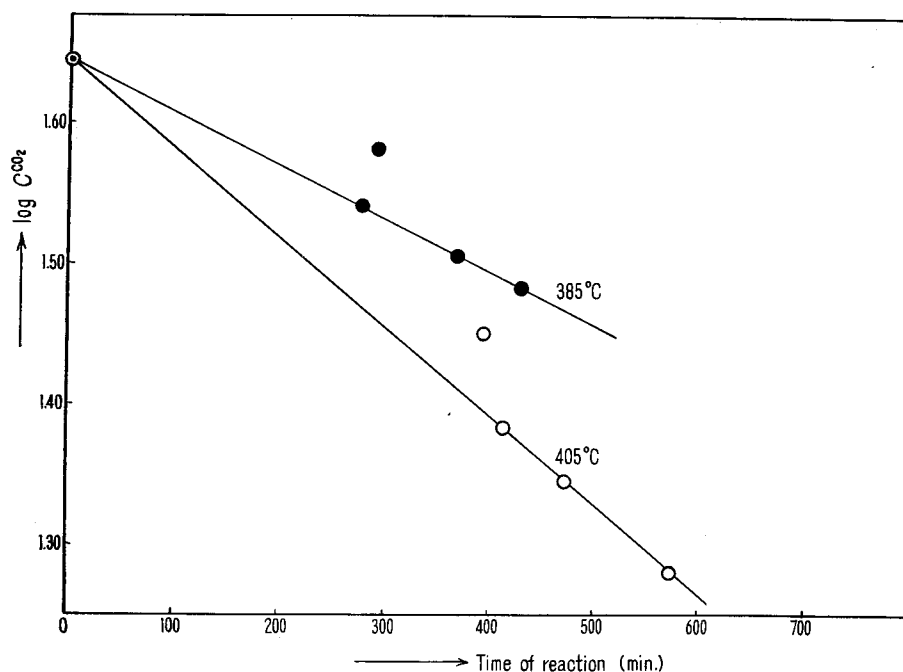


Fig. 7. Direct exchange reaction between CO and CO_2 , $\log C^{\text{CO}_2}$ vs. time of reaction.

Fig. 8 to 11 shows the plots of C^{CO_2} and $\log P^{\text{CO}_2}$ against time of reaction respectively, from which the values of $d \ln P^{\text{CO}_2}/dt$ and dC^{CO_2}/dt in Eq. (11) at initial state of reaction (1) have been determined with the aid of prism⁷⁾ as shown in Table 1 to 4.

Fig. 12 shows the value of ν_r as calculated according to Eq. (11) at the initial stage of water gas shift reaction of each run^{*)}. This result shows that ν_r is unity except that of run 1, which appreciably exceeds unity.

This is explicable on the ground that the direct exchange was observed directly after run 2 and 3 respectively at temperature of 385°C and 405°C,

* cf. page 172.

On the Mechanism of Water Gas Shift Reaction II

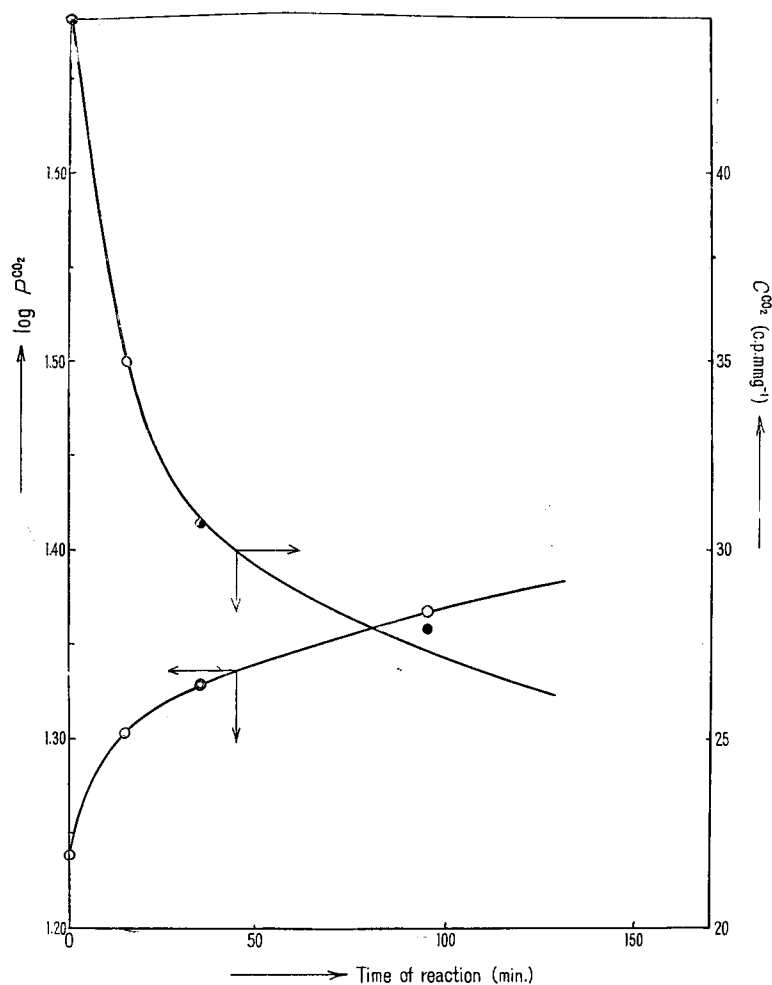


Fig. 8. Log P^{CO_2} and C^{CO_2} vs. time of reaction, run 1.

the latter results being used for the correction of run 1. As mentioned previously, the activity of catalyst was not completely constant but decayed slowly along with the repetition of runs. It is hence possible that the direct exchange proceeds rapider in the case of run 1 than observed directly after run 3 or the correction applied to the result of run 1 was too small. We see on the other hand that both the numerator and the denominator of Eq. (11) are negative

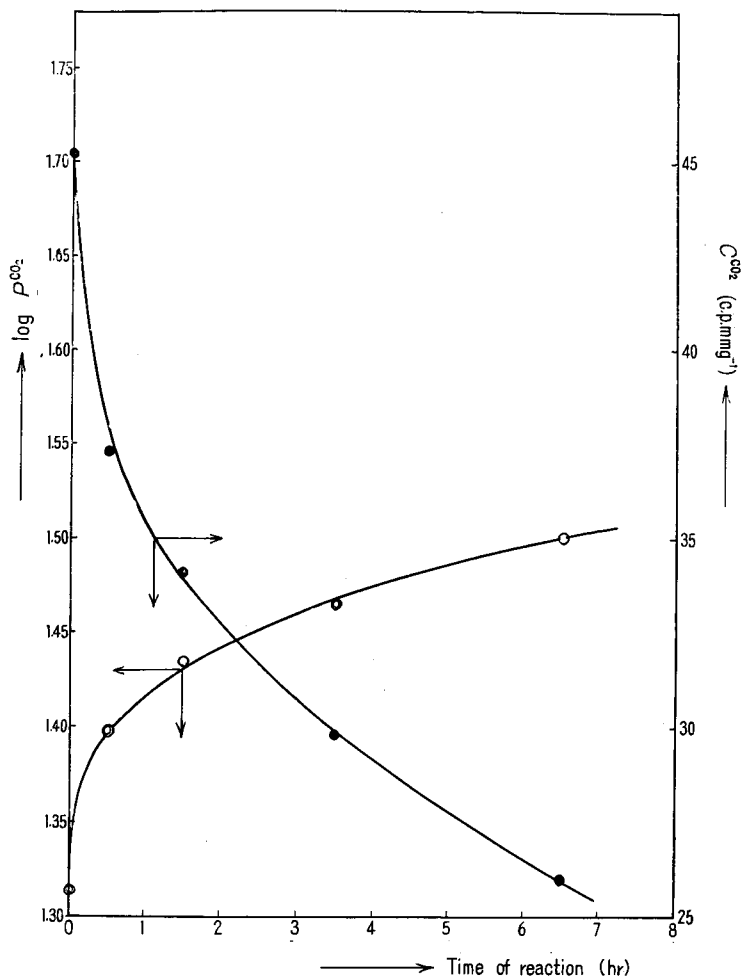


Fig. 9. $\log P^{\text{CO}_2}$ and C^{CO_2} vs. time of reaction, run 1.

and the argument of the denominator is written as

$$1 - \frac{|C^{\text{CO}} - C^{\text{CO}_2}| \times |d \ln P^{\text{CO}_2}/dt|}{|dC^{\text{CO}_2}/dt| - |P_0^{\text{CO}_2}/P^{\text{CO}_2}| \times |(d \ln C^{\text{CO}_2}/dt)_{0,\text{ex}}| \times |C^{\text{CO}_2} - C^{\text{CO}}|};$$

too small a value of $|(d \ln C^{\text{CO}_2}/dt)_{0,\text{ex}}|$ makes now the absolute value of the second term of the above expression too small, hence the absolute value of the

On the Mechanism of Water Gas Shift Reaction II

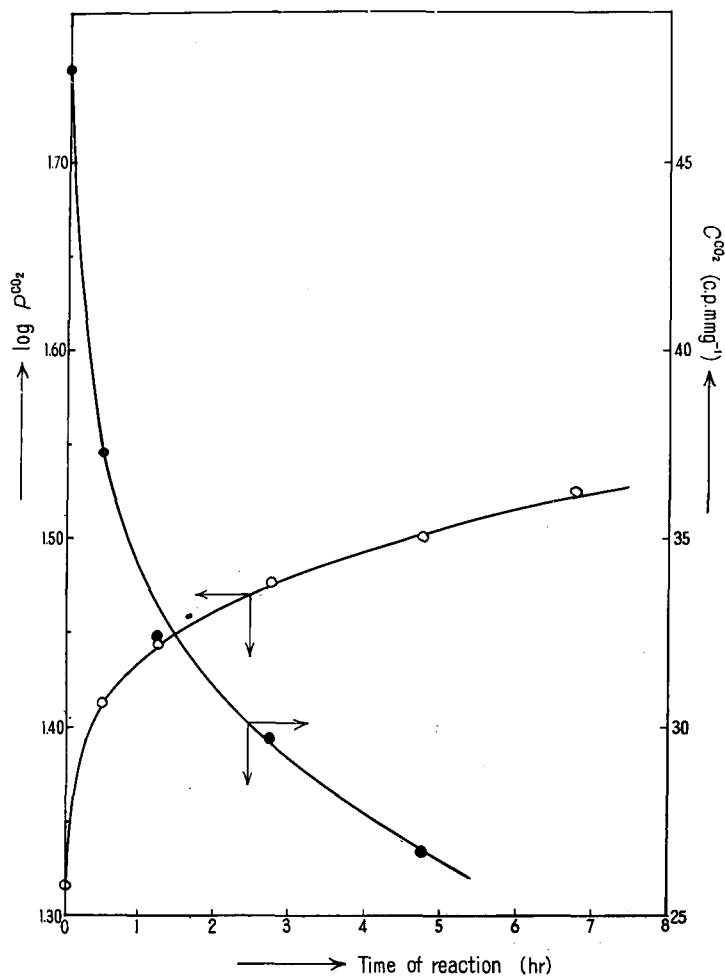


Fig. 10. $\log P^{\text{CO}_2}$ and C^{CO_2} vs. time of reaction, run 3.

denominator of Eq. (11) too small or the calculated value of ν_r too large. It is hence concluded that run 1 gives the upper limit to the ν_r -value.

At any rate it leaves little doubt with regard to the conclusion that ν_r is of the order of magnitude of unity.

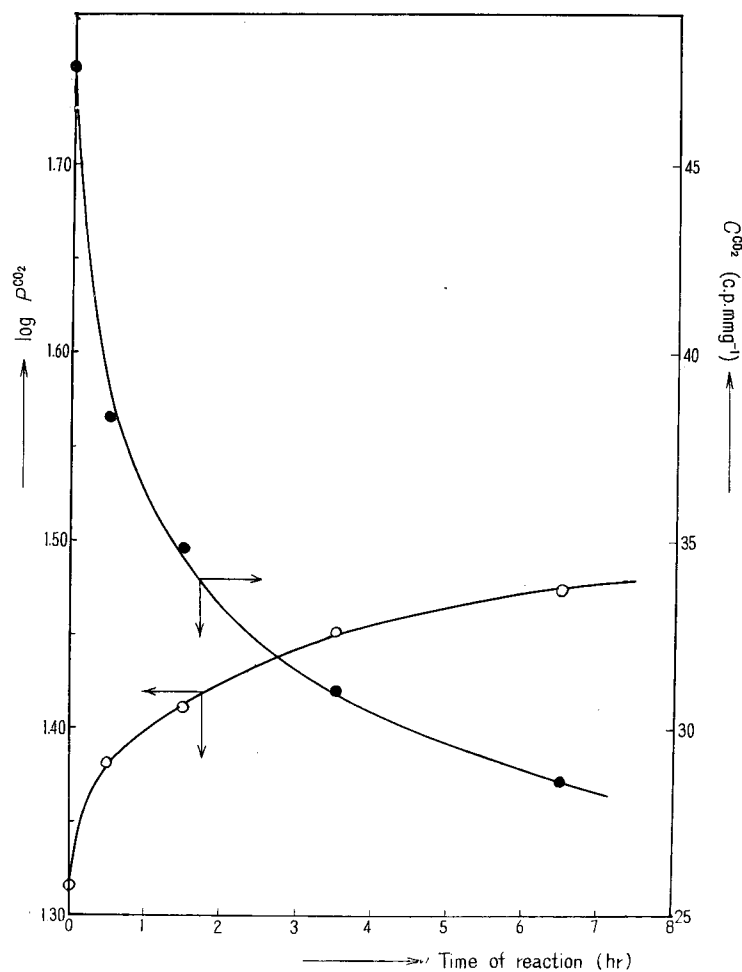


Fig. 11. $\log P^{\text{CO}_2}$ and C^{CO_2} vs. time of reaction, run 4.

V. Discussion

Table 5 shows different sequences, I, II and III of steps, stoichiometric number ν of respective constituent steps and the ν_r -value to be observed by using the isotope indicated at the top of each column in case where the step on the same line is rate-determining. Sequence I is the reproduction of sequence 2. If, for instance, step $\text{H}_2\text{O} \rightarrow 2\text{H(a)} + \text{O(a)}$ is rate-determining, ν_r to

On the Mechanism of Water Gas Shift Reaction II

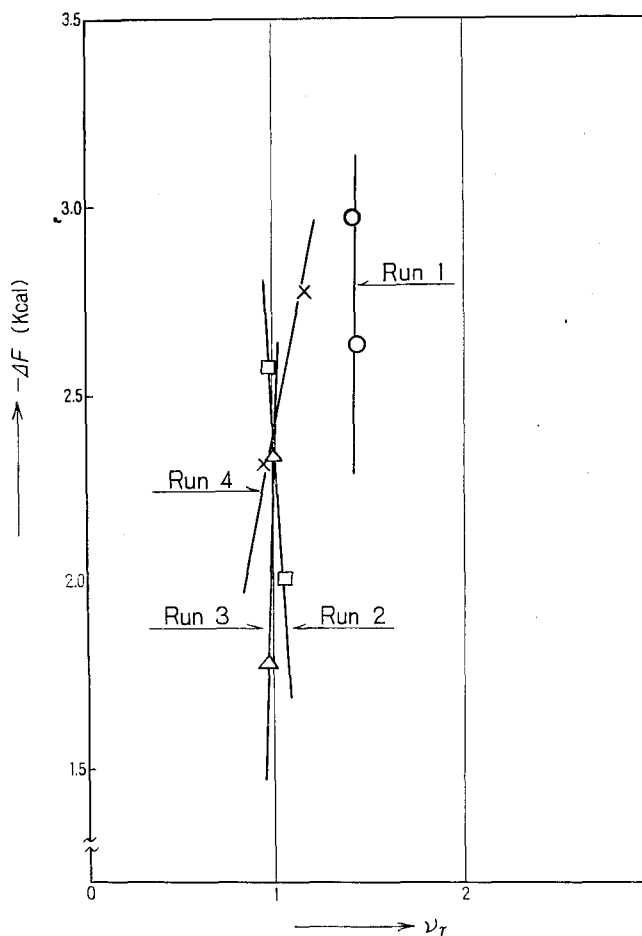


Fig. 12. Observed stoichiometric number of rate-determining step *vs.* affinity.

be observed is unity or ∞ according as deuterium or radioactive carbon is used as tracer. Present authors have previously found ν_r unity by using deuterium as tracer⁵⁾. It has now been found that ν_r is unity as well by using radioactive carbon, which excludes sequence I definitely.

These experimental results fit in with sequence II or III as seen from Table 5, provided that the last step in each sequence determines the rate. This conclusion is in conformity with the mechanism advanced by KAGIYA,

TABLE 5. Values of stoichiometric number ν_r of rate-determining step.

Sequence	Constituent step	stoichiometric number			
		Theoretical ν	Observable ν_r		
			D	C ¹⁴	O ¹⁸
I	$\text{H}_2\text{O} \rightarrow 2\text{H}(\text{a}) + \text{O}(\text{a})$	1	1	∞	1
	$\text{CO} + \text{O}(\text{a}) \rightarrow \text{CO}_2$	1	∞	1	1
	$2\text{H}(\text{a}) \rightarrow \text{H}_2$	1	1	∞	∞
II	$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(\text{a})$	1	1	∞	1
	$\text{CO} \rightarrow \text{CO}(\text{a})$	1	∞	1	1
	$\text{H}_2\text{O}(\text{a}) + \text{CO}(\text{a}) \rightarrow \text{H}_2 + \text{CO}_2$	1	1	1	1
III	$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}(\text{a})$	1	1	∞	1
	$\text{H}_2\text{O}(\text{a}) + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$	1	1	1	1

SENO and FUKUI⁹), as well as with the LANGMUIR-HINSHELWOOD and the RIDEAL-ELEY mechanisms but conflicts with TEMKIN's⁹) or TAMARU's¹⁰) mechanism, which requires $\nu_r = \infty$ in case of deuterium or radioactive carbon respectively used as tracer.

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