Kinetics and Isotope Effect in Methanol Synthesis at Low Pressures

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The methanol synthesis has been the object of many investigations, among which a few works have been devoted to the kinetics of the reaction. The kinetic equations thus obtained are different from each other in form:

by Temkin et al. at low pressures:[1]

$$r=kC_{H_2}C_{CO}^{0.6}/C_{CH_3OH} \qquad (1)$$

by Natta et al. at high pressures:[2]

$$r=kP_{H_2}^{2}\cdot P_{CO}/(A+BP_{CO}+CP_{H_2}+DP_{CH_3OH})^{3} \qquad (2)$$

by Ogino et al. at high pressures[3]:

$$r=k(P_{H_2}^{2}\cdot P_{CO})^{0.7} \qquad (3)$$

although they may all be approximated to (3) or (1) in nature. In consequence, different fundamental postulates of the rate-determining step in the synthesis of methanol have been suggested, that is, the adsorption of carbon monoxide or hydrogen for (1), the surface reaction for (2), and the desorption of the product methanol for (3).

Such disagreement in interpreting the kinetics of the same reaction is suspicious, since the equations are all similar in nature. In this connection, the isotope effect on the reaction rate has been useful in identifying the rate-determining step of many reactions. The effect in methanol synthesis, however, has not been reported. Corval and Viallard[4] studied the synthesis of heavy methanol CD_3OD, but they didn't compare the rate with that of light methanol. It was, therefore, decided to undertake an investigation of the isotope effect in methanol synthesis. The work was done in the vicinity of atmospheric pressure with a reactant mixture of varying compositions.

Experimental

Reagents.—Cylinder hydrogen was passed over a platinum catalyst to remove any oxygen and then dried with liquid nitrogen. Deuterium gas was prepared by the reaction of heavy water of 99.7% D, which had been supplied by the Showa Denko Co., with a magnesium ribbon at 400 to 450°C. Carbon monoxide was prepared by the decomposition of sodium formate with concentrated sulfuric acid and was passed over sodalime and dried with liquid nitrogen. The catalyst was supplied in a partially-reduced state by the Government Chemical Industrial Research Institute, Tokyo, and contained zinc, chromium, and copper in the atomic ratio of 1 : 0.49 : 0.16.[5] The catalyst was used as particles of 1 to 2 mm. The reduction of the catalyst was carried out with the reactant gas of excess hydrogen in situ at 250°C for 12 hr.

Experimental Procedures. — The experiments were carried out at a constant pressure in a closed flowing system, which is shown schematically in Fig. 1. The synthesis mixtures were circulated on the catalyst at various velocities by means of an all-glass electromagnetic pump. In order to preheat the gas mixture, the reaction tube was packed 5 cm. thick with glass beads over the catalyst bed (10 mm. thick), through which the gas stream flowed downwards. The catalyst was placed on a fritted glass plate of a coarse grade. A thermocouple well was inserted through the glass beads bed and the catalyst bed. The reaction tube was

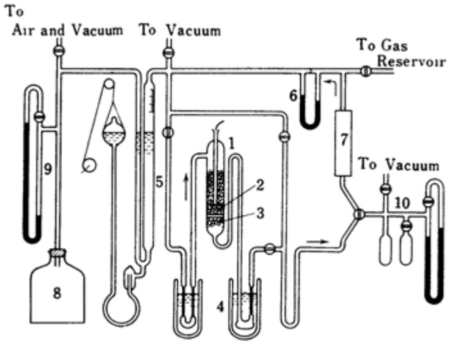

Fig. 1. Apparatus.

1 Reactor
2 Catalyst bed
3 Inert packing as a bed support
4 Traps
5 Buret
6 Flow meter
7 Circulating pump
8 A tank of 50 l. as a buffer
9 Manometer
10 Manometer for vapor pressure measurement

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[1] V. M. Cherednichenko and M. I. Temkin, *Zhur. Fiz. Khim.*, **31**, 1072 (1957).

[2] G. Natta, P. Pino, G. Mazzanti and I. Pasquon, *LaChimica e L'Industria*, **35**, 705 (1953).

[3] H. Uchida and Y. Ogino, This Bulletin, **31**, 45 (1958).

[4] M. M. Corval and M. R. Viallard, *Bull. soc. chim. France*, **50**, 484 (1954); *J. chim. phys.*, **51**, 619 (1954).

[5] Y. Ogino, M. Oba and H. Uchida, This Bulletin, **33**, 358 (1960).

placed in an aluminum block furnace, and the temperature was controlled within ±0.5°C by means of a thermoelectric temperature controller. The temperature difference between the two ends of the catalyst bed was within 0.2°C during the measurement. The two traps, which were placed before and after the reaction tube, were put into the same liquid-nitrogen bath, and the liquid level of the bath was adjusted to a certain position during the measurement. According to Temkin et al., the satisfactory trapping of methanol vapor with liquid nitrogen is difficult because the vapor tends to form aerosol. In order to avoid this difficulty, the trap next to the reaction tube shown in Fig. 1 was designed so as to give a low linear gas velocity; that is, the trap was made from a tube 18 mm. in inner diameter at the bottom corresponding to the liner velocity of 0.1 cm./sec. at the liquid nitrogen temperature for the gas velocity of 3 l. N. T. P/hr. It was confirmed by the absence of deposition in the other trap that the trap was satisfactory for condensing the methanol vapor.

The reaction rates were measured by following the volume decrease with the gas burette. The volume of the closed system was about 300 ml. besides the burette volume of 70 ml. The reaction products, a mixture of methanol and carbon dioxide collected in the trap during the rate measurements, were subjected to vapor pressure measurements at 0°C and −78°C; cf. the right section of the diagram Fig. 1. The amounts of both products were estimated from these quantities. The respective rates of the formation of both products were calculated as the rates of the volume decrease of the reaction system multiplied by a conversion factor which will be shown later.

Results

In the preliminary experiments on the synthesis at 160 to 230°C, it was shown that the carbon dioxide formation was remarkable at higher temperatures, while the reaction rate was too slow to observe at temperatures lower than 180°C. Accordingly, the measurement of the temperature coefficient of the reaction rate was abandoned and the reaction temperature was fixed at 180°C throughout the experiments.

Since the carbon dioxide formation was not negligible even at 180°C, the reaction path of the formation ought to be assigned in order to give a correction to the reaction rate of methanol synthesis. There can be considered to be three possible ways of carbon dioxide formation:

i) $2CO = CO_2 + C$

ii) $2CO + 2H_2 = CO_2 + CH_4$

iii) The oxidation of CO by the catalyst

In the present analysis, reaction ii was excluded because of the absence of methane in the circulating gas after several hours of reaction. The detection of methane was carried out by gas chromatography. Reaction iii was improbable because the catalyst was, prior to use, thoroughly reduced at a higher temperature, 250°C, than the reaction temperature, 180°C, using the reactant gas, and because no degradation of catalytic activity to form carbon dioxide was observed. Consequently, it was postulated that the carbon dioxide was formed via reaction i. Thus, the rate of the volume decrease due to the formation of methanol and of carbon dioxide, r_M and r_C (N ml./hr.) respectively, was estimated by the equation:

$$r_M = 3N_M r_A / (3N_M + 2N_C) \qquad (1)$$

$$r_C = 2N_C r_A / (3N_M + 2N_C) \qquad (2)$$

where r_A is the measured rate of volume decrease, N ml./hr., and N_M and N_C are the amounts of methanol and carbon dioxide (mole) formed in each run, each of which was continued for four hours. Since the per-pass conversions were very low and within 5% of the equilibrium conversions, the estimated rate, r_M or r_C, is the initial rate.

The effects of total pressure, P, on r_M and r_C are shown in Fig. 2 for a constant molar ratio $n(=H_2/CO$ or $D_2/CO)$. Figure 3 shows the variations of r_M and r_C with n at atmospheric pressure. All the experimental data are the time averages, in each run carried out at a fixed condition for four hours. The optimum methanol formation appears at a n value of around 2.

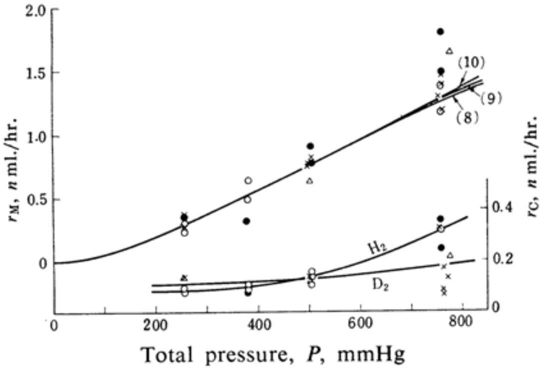

Fig. 2. Total pressure dependence of the rates with stoichiometric mixture.

○ H_2 s. v. 900 ● H_2 s. v. 1800

× D_2 s. v. 900 △ D_2 s. v. 1800

As may be seen in Fig. 2, no marked influence was observed on r_M by changing the space velocity from 900 to 1800. Since the variation in space velocity should give rise to a different value of methanol vapor pressure in the catalyst bed, it seems that methanol has no effect on r_M under the present experimental conditions.

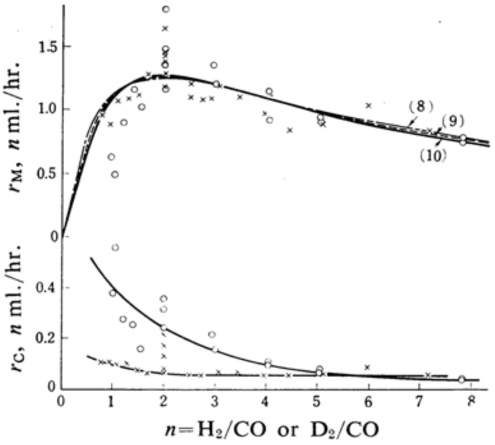

Fig. 3. Variation of the rates with gas composition under 1 atm.
180°C 1 atm s. v.: 900 hr^{-1}

The deuterium isotope effect in methanol synthesis was not observed, as can be seen in Fig. 2, and Fig. 3; that is, both plots for protium and deuterium are distributed along the same line and show no systematical deviation from each other. This result was confirmed by changing the reactant gases in the order; H–D–H–D–D.

On the other hand, the isotope effect was found in the carbon dioxide formation at higher concentrations of carbon monoxide. The amount of carbon dioxide formed was near 20% (mole) of methanol in most runs, the highest value being 30%.

A Kinetic Analysis of the Results

A kinetic equation which incorporates the experimental results shown in Fig. 2 was selected in the following way. A general form, expressed with the total pressure, P,

$$r_M=kP^l/(1+aP^m)^s \tag{3}$$

was considered, and the possible combinations of l, m and s were tested one by one, assigning every half interger from 0.5 to 3 for l and m, and every integer from 1 to 3 for s. Equation 3 was transformed into:

$$1/k^{1/s}+aP^m/k^{1/s}=(P^l/r_M)^{1/s} \tag{4}$$

and the linearity of P^m against $(P^l/r_M)^{l/s}$ was examined.

TABLE I. SUITABLE COMBINATIONS OF l, m, AND s

No.	1	2	3	4	5	6
l	2	2.5	3	2.5	3	3
m	1	1	1	1.5	1.5	2
s	2	2	2	1	1	1

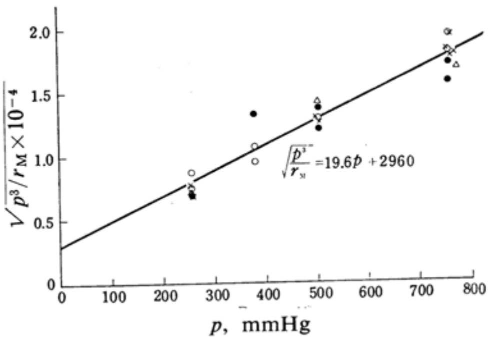

Fig. 4

The suitable combinations thus found were as shown in Table I.

However, the best fit was obtained in Nos. 2 and 3. The plots in No. 3 are exemplified in Fig. 4.

Equation 3 rewritten in terms of the partial pressures, p_{H_2} and p_{CO}, and of n, assuming a first-order dependence on p_{CO}, i. e. the kinetic term of the $k'p_{H_2}{}^{l-1}p_{CO}$ form. For example, with $m=1$, the rewritten equation is:

$$r_M=k'{}_{H_2}{}^{l-1}p_{CO}/(1+a_1p_{H_2}+a_2p_{CO})^s \tag{5}$$

$$=\frac{k'n^{l-1}P^l/(n+1)^l}{[1+(na_1+a_2)P/(n+1)]^s} \tag{6}$$

where $k'=k(n+1)^l/n^{l-1}$.

Equation 6 was transformed to:

$$(1+a_2P)+(1+a_1P)n$$
$$=[k'n^{l-1}P^l(n+1)^{l/s}r_M]^{1/s} \tag{7}$$

The linear relation of the right side of Eq. 7 against n was examined for the l-m-s combinations shown in Table 1, using a k' value obtained by the linear relation of Eq. 4. Any combination which gave a negative value for a_1 or a_2 was discarded. Thus, the suitable combinations in these plots were Nos. 1, 2 and 3 of Table I, in all of which $m=1$ and $s=2$. In other words, these equations are as follows:

$$r_M=k'p_H\,p_{CO}/(1+a_1p_{H_2}+a_2p_{CO})^2 \tag{8}$$

$$r_M=k'p_{H_2}{}^{1.5}p_{CO}/(1+a_1p_{H_2}+a_1p_{CO})^2 \tag{9}$$

$$r_M=k'p_{H_2}{}^2p_{CO}/(1+a_1p_{H_2}+a_2p_{CO})^2 \tag{10}$$

The plots in No. 3 are exemplified in Fig. 5, where some systematic deviation is observed in the lower range of n for only the protium series. This deviation was also observed for the other l-m-s combinations.

The k', a_1 and a_2 constants were recalculated by the least squares method with all the data shown in Figs. 2 and 3, excepting those obtained with n values lower than 2 in the case of protium. The best values thus obtained are given in Table II.

TABLE II. BEST VALUES OF k', a_1 AND a_2

Equation	k'		a_1		a_2	
	$(2H_2+CO)N$ ml.*/hr. 2.493 g. cat.	mol.*/hr. g. cat.	$mmHg^{-1}$	atm^{-1}	$mmHg^{-1}$	atm^{-1}
(8)	$(3.09\pm0.28)\times10^{-5}$	$(1.06\pm0.09)\times10^{-4}$	$(4.93\pm0.97)\times10^{-4}$	0.375 ± 0.073	$(2.11\pm0.21)\times10^{-3}$	1.60 ± 0.16
(9)	$(4.35\pm0.64)\times10^{-6}$	$(4.13\pm0.61)\times10^{-4}$	$(2.40\pm0.29)\times10^{-3}$	1.83 ± 0.22	$(3.70\pm0.45)\times10^{-3}$	2.82 ± 0.34
(10)	$(1.36\pm0.50)\times10^{-6}$	$(3.56\pm1.30)\times10^{-3}$	$(0.99\pm0.21)\times10^{-2}$	7.51 ± 1.57	$(0.91\pm0.21)\times10^{-2}$	6.95 ± 1.57

* These dimensions are consistent with those of r_M.

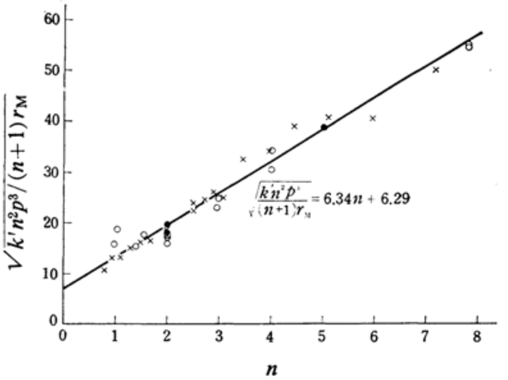

Fig. 5

The rate of methanol formation was calculated using Eqs. 8, 9 and 10 and are shown in Figs. 2 and 3 with lines. These lines overlap each other, and the experimental points are located along them, although some deviations are clearly seen in the lower range of n values.

Discussion

Kinetic Equation.—The range of experimental conditions was not wide enough to discriminate a single rate equation. The three equations finally reached all have the adsorption terms of both hydrogen and carbon monoxide in accordance with the equation of Natta et al., although the exponent to the adsorption term, s, is different. The adsorption term of methanol may disappear because of the low conversion in the present experiment.

The rates of methanol formation under elevated pressures were estimated using the above three equations. The estimated rate with Eq. 8 was independent of the pressure above 20 atm., but not with Eqs. 9 and 10. This independence of the reaction pressure is contradictory with the established fact of pressure dependency in the methanol synthesis. Hence, Eq. 8 may be abandoned.

The kinetic terms $p_{H_2}^{1.5}p_{CO}$ and $p_{H_2}^{2}p_{CO}$ of Eqs. 9 and 10 respectively resemble with those of Natta et al. and of Ogino et al.

If the following elementary reactions are assumed to constitute the methanol synthesis:

$$CO + H_2 \rightarrow HCHO \tag{I}$$

$$HCHO + H_2 \rightarrow CH_3OH \tag{II}$$

then Eq. 10 conforms to the postulate that reaction II is rate-determing, because the partial pressure of HCHO, the reactant of reaction II, is expressed as $K_I p_H \cdot p_{CO}$, where K_I is the equilibrium constant of reaction II.

For Eq. 9, the reaction scheme may be as follows:

$$H_2 \rightleftarrows 2H(a) \tag{III}$$

$$CO + 2H(a) \rightarrow CH_2O(a) \tag{IV}$$

$$CH_2O(a) + H(a) \rightarrow CH_3O(a) \tag{V}$$

$$CH_3O(a) + H(a) \rightarrow CH_3OH \tag{VI}$$

with reaction V being rate-determining.

The discrimination of the above two schemes must auait further investigation.

Isotope Effect.—The fact that no isotope effect is found in the methanol formation may give rise to the view that the adsorption of carbon monoxide is rate-determining. However, the rate equations obtained here and by other investigators suggest that this view is by no means valid, because the kinetic term of the rate equations clearly depends on the hydrogen pressure. In other words, the rate equations suggest a rate-determining step in which hydrogen or a hydrogen-containing species is involved. A complete interpretation of the above discrepancy can follow only further investigation.

The hydrogen isotope effect was observed in the carbon dioxide formation, particularly in the higher concentrations of carbon monoxide, where the deviation from the rate equation for methanol formation was also observed. These observations may suggest that the carbon dioxide formation takes place on an active site different from that of the methanol formation. Since hydrogen is not involved in the reaction path assumed for the carbon dioxide formation, the observed isotope effect must be ascribed to the higher surface coverage with deuterium, which suppresses the carbon dioxide formation. However, such an interpretation of the results should be subjected to further investigation.

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