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Kinetics of Vapor-Phase Oxidation of Methanol on Reduced Silver Catalyst

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The kinetics of oxidation of methanol to formaldehyde and carbon dioxide has been studied in the temperature range 264–290°C over a silver catalyst, using a differential flow reactor operating at a low conversion level under atmospheric pressure. The following rate equation, derived on the basis of a steady-state adsorption model, was found to explain the experimental data satisfactorily.

$$r = \frac{2k_o k_m p_{O_2}^{\frac{1}{2}} p_m}{k_m p_m + 2k_o p_{O_2}^{\frac{1}{2}}}$$

From the rate constants k_o and k_m, the energies of activation of the two processes were determined.

INTRODUCTION

The mechanism of oxidation of CH_3OH to HCHO, though apparently simple, is in fact complex and there is much difference of opinion regarding the function of O_2. Thomas (*1*) suggested that the oxidation process in the presence of silver catalyst is primarily dehydrogenation and that the function of O_2 is to react with the liberated H_2 so as to maintain the equilibrium of the dehydrogenation process. He also supposed O_2 to be responsible for keeping the catalyst active and maintaining the necessary temperature.

On the other hand, according to Vlodavets *et al.* (*2*), the reaction is supposed to occur between O_2 adsorbed on the catalyst and methanol in the gas phase. Any other side reaction occurs in the gas phase, and O_2 is the only species to be adsorbed on the catalyst surface.

Ever since the publication of the results of oxidation of hydrocarbons on vanadium oxide catalyst by Mars and van Krevelen (*3*), the two-step "redox mechanism" propounded by them has been subjected to tests by various workers (*4*, *5*) and has been found to be very helpful in explaining the rates and the mechanism of the oxidation of methanol, using pure or mixed oxide catalysts. This mechanism assumes the direct reaction of lattice oxygen with methanol in the gas phase.

On the other hand, Graydon *et al.* (*6*, *7*), and Downie *et al.* (*8*) have utilized the Hinshelwood concept of steady-state concentration of reactants on the catalyst surface rather than an equilibrium concentration to deduce a similar rate equation which could explain the oxidation reactions of aromatic hydrocarbons on oxide catalysts.

The essential difference between the two concepts lies in the assumption of direct participation of lattice oxygen in the former case, and the reaction of adsorbed O_2 on the catalyst surface in the latter one. However, the rate equations derived in both ways are synonymous.

In the present study, the oxidation of CH_3OH over reduced Ag catalyst has been carried out at a low conversion level (so that the effect of products on the rates could be neglected) and under a condition of negligible diffusional effects.

A rate equation based on the steady-state-adsorption model has been deduced and found suitable for explaining the experimental results satisfactorily.

NOMENCLATURE

r_{CH_2O}	rate of formation of CH_2O (moles $hr^{-1}g^{-1}$ catalyst)
r_{CO_2}	rate of formation of CO_2 (moles $hr^{-1}g^{-1}$ catalyst)
r	total rate $= r_{CH_2O} + r_{CO}$
k_o	specific rate constant for adsorption of O_2 (moles hr^{-1} g^{-1} atm^{-1})
k_m	specific rate constant for reaction between adsorbed O_2 and alcohol (moles hr^{-1} g^{-1} atm^{-1})
p_{O_2}	partial pressure of O_2
p_m	partial pressure of CH_3OH
α	Mars and van Krevelen stoichiometric number, (moles of O_2 required per mole of methanol reacted)
m	order of reaction with respect to methanol concentration
n	order of reaction with respect to oxygen concentration
T	temperature in absolute scale
F_A	feed rate of reactant A (moles/hr)
x_A	fractional conversion of reactant A (moles converted/moles fed)
W	weight of the catalyst in grams

EXPERIMENTAL PROCEDURE

A. Catalyst. The catalyst was obtained by heating Ag_2O in a platinum crucible and in an argon atmosphere at 500–600°C. The oxide, being highly unstable towards heat, lost all O_2, and metallic Ag was obtained which was greyish-white in color. The starting Ag_2O was obtained as a precipitate by treating (*N*) NaOH (carbonate free) solution with (*N*) $AgNO_3$ solution. The precipitate was washed free of alkali, NO_3^- and Na^+ and was dried at 70°C for about 20 hr (*9*).

B. Materials used. Methanol (B.D.H. Analar) was purified via the formation and subsequent hydrolysis of CH_3MgI and finally distilled at 64.7°C. This alcohol was used as the starting material.

$AgNO_3$: E. Merck Analar grade was used.

Argon (99.55%): O_2 was removed by passing through copper gauze heated to 400°C.

Apart from these, the reagents used for the analyses of reactants and products were of analytical grade.

C. Apparatus. The apparatus was almost the same as that used by Bhattacharyya *et al.* (*5*) with only a few minor modifications. In the present study, a glass preheater coil was wound round the catalyst tube. The reactor was a Pyrex glass tube of length 13 in. and i.d., 0.8 in. It had two zones, (a) a preheater zone comprised of a packing of Pyrex glass beads and (b) a reactor zone where the catalyst was secured between two plugs of Pyrex glass wool. The system operated under normal atmospheric pressure (generally 76 cm Hg). After an initial lapse of 1.5 hr for ensuring attainment of steady-state condition, the actual oxidation run was conducted for 15 min during which the liquid and gaseous products were collected.

D. Analytical procedure. Formaldehyde was estimated by the iodimetric method (*10*) and unconverted methanol was estimated by the $K_2Cr_2O_7$–H_2SO_4-oxidation method (*11*). Carbon dioxide was absorbed in standard $Ba(OH)_2$ solutions, and by titrating the excess alkali, the amount of CO_2 was determined (*12*).

Thermodynamic calculations of the oxidation of methanol by air have been performed in detail by Fowlie and Jones (*13*). In connection with the present work, the equilibrium constants of the probable reactions have been calculated for the reaction temperatures and are shown in Table 1.

The general rate equation $r_A = F_A \cdot dx_A/dW$ was used for the calculation of the rates. The rate was expressed as

$$r_i = \frac{\text{No. of moles of product } i \text{ formed}}{(\text{time in hr}) \times \text{g (catalyst wt in g)}}.$$

The total rate can be expressed at $r = \Sigma r_i$. In this particular case, the total rate was the sum of the rates of production of CH_2O and CO_2, i.e.,

$$r = (r_{CH_2O} + r_{CO_2}).$$

TABLE 1
VALUES OF k_p AT VARIOUS TEMPERATURES

	Temp (°K)		
Reactions	537	554	563
(i) $CH_3OH \rightleftharpoons CH_2O + H_2$	2.23×10^{-3}	4.24×10^{-3}	5.79×10^{-3}
(ii) $CH_3OH + \frac{1}{2}O_2 \rightleftharpoons CH_2O + H_2O$	4.20×10^{18}	1.44×10^{18}	0.83×10^{18}
(iii) $CH_3OH + \frac{1}{2}O_2 \rightleftharpoons CO_2 + 2H_2O$	4.25×10^{4}	2.80×10^{4}	2.23×10^{4}
(iv) $CH_2O + O_2 \rightleftharpoons CO_2 + H_2O$	2.08×10^{2}	2.10×10^{2}	2.12×10^{2}

No correction was made for the partial pressures of methanol, water, or oxygen due to the formation of the products; because that small amount of products formed in a differential reactor, operating under a very low conversion level, would not alter these values of considerable amount.

RESULTS AND DISCUSSION

Because this study was concerned with the chemical aspects of the process, all the runs were taken at steady states and under the condition of negligible external and internal diffusion effects (*15*). The alcohol was diluted with water so as to avoid the high heat effects of the reaction, which incidentally was also the reason of choosing a narrow range of temperature of our studies. The uncatalyzed decomposition and oxidation of methanol at the temperature range chosen was nil, and as such, the catalytic rate was not corrected. The only products obtained were formaldehyde and CO_2 under the present condition. No carbon monoxide or formic acid could be detected.

Figure 1 shows the effect of variation of

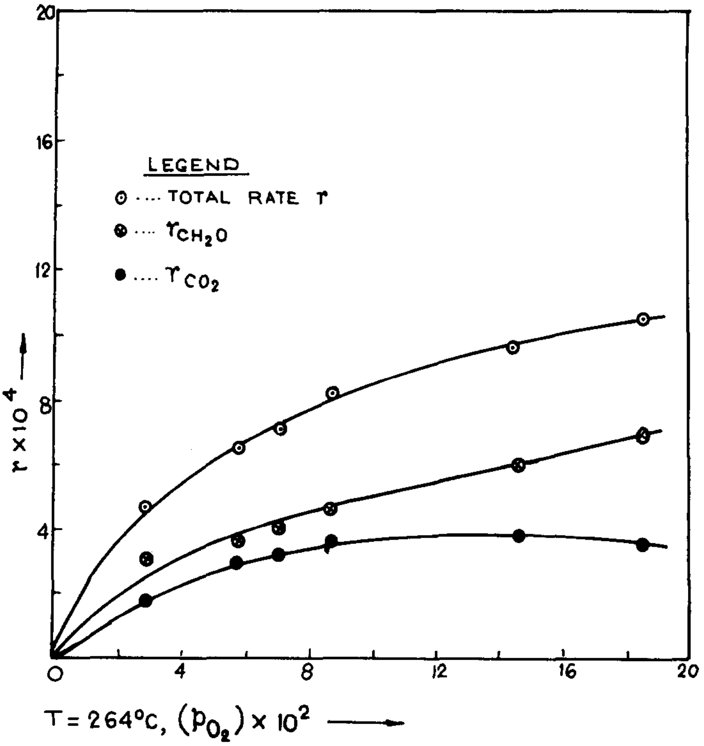


FIG. 1. Effect of p_{O_2} on rates.

partial pressure of O_2 on rate, at 264°C, while p_m, p_{H_2O}, and other kinetic parameters are constant. Figure 2 shows the variation of rate with p_m, keeping all the other kinetic parameters constant. Identical sets of data were obtained and plotted in the same way at 281 and 290°C, so as to see the effect of temperature on the rates and to calculate the energies of activation. The effect of p_{H_2O} on the rate is demonstrated in Fig. 3 and log r vs log p_{H_2O} is plotted in Fig. 4.

In case of variation of r with respect to variation of p_{O_2} and p_m, the rate sharply increases at the lower values of p_{O_2} or p_m and gradually tends to attain a constant value; while in case of variation of p_{H_2O}, the rate decreases sharply at the lower value region of p_{H_2O} and attains a constant value quickly (Fig. 3).

The kinetic studies on methanol oxidation carried out by various authors on V_2O_5 and other mixed oxides like $Fe_2(MoO_4)_3$ (*4*) and MnO_2–Fe_2O_3 (*16*) have been explained by the Mars and van Krevelen mechanism (*3*). This mechanism assumes a two-stage redox process where the gaseous alcohol reacts directly with the lattice oxygen which is again replenished by the atmospheric O_2. Since oxidation of the reduced catalyst is slower, it has the greater effect on the rate (*4*).

With a very delicate difference in assumptions embodied in the adsorption of O_2 on the catalyst surface, Graydon *et al.* (*6, 7*) have applied the modified Hinshelwood mechanism to explain their kinetic results of vapor-phase oxidation of benzene over vanadium oxide catalysts. This mechanism has also been studied by Downie (*17*) *et al.* and found to explain their kinetic results also.

The above mechanism, first applied by Graydon, at present known well as the "steady-state-adsorption model" (S.S.A.) (*17*), has been applied by the present authors to deduce a rate equation which has been found to explain the kinetic results, in the range of investigation, excellently. The assumptions embodied in the deduc-

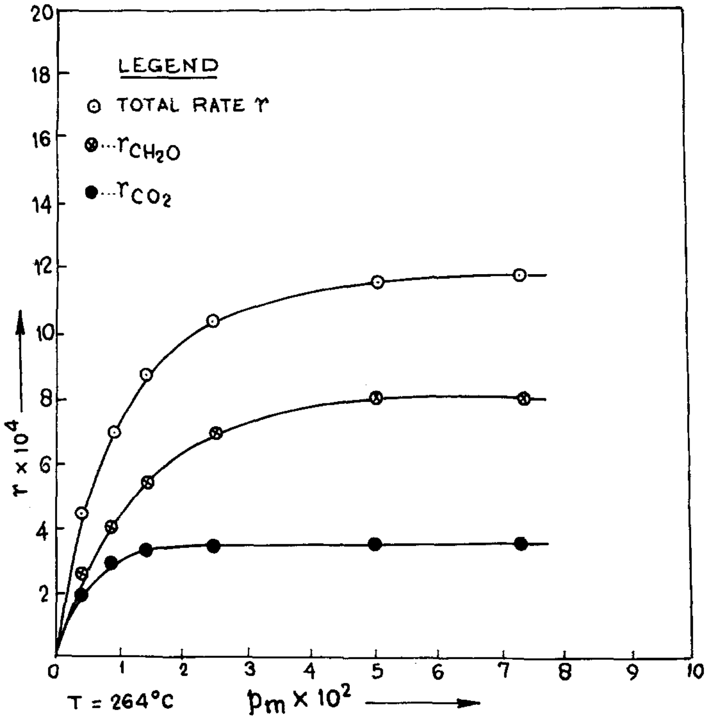


FIG. 2. Effect of p_m on rates.

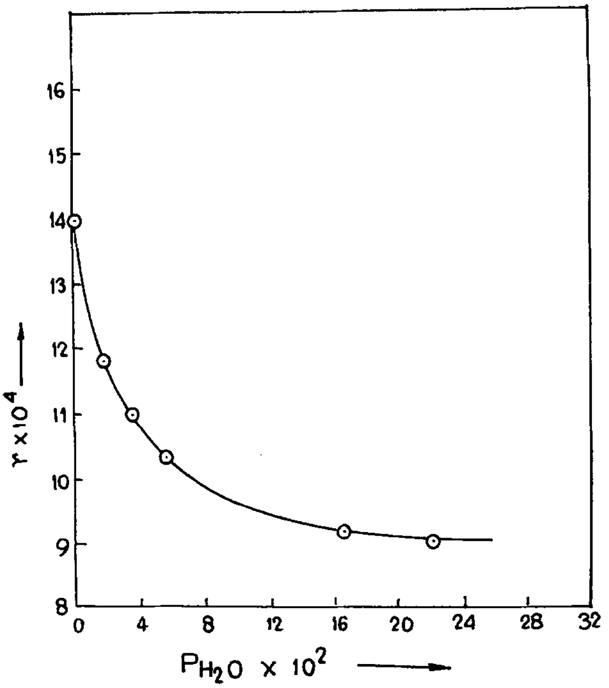


FIG. 3. Effect of (p_{H_2O}) on rate.

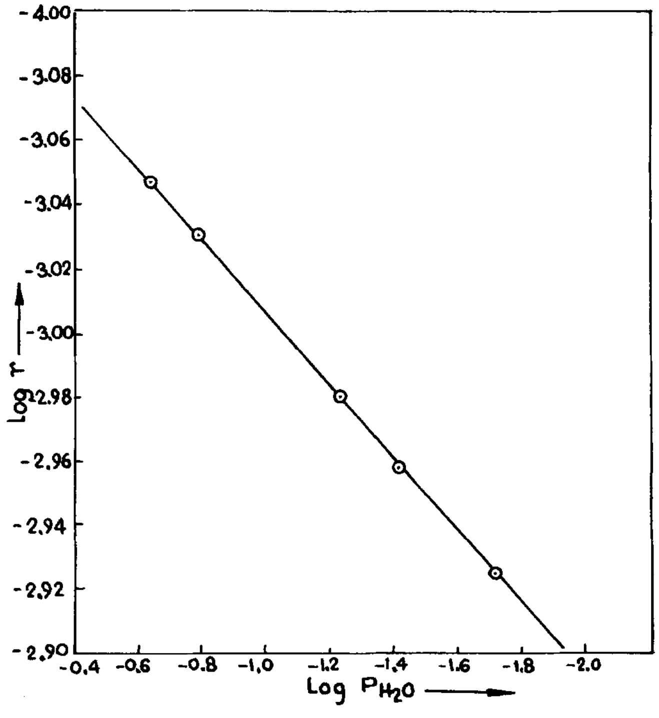


FIG. 4. Plot of log r vs log p_{H_2O}.

tion of the rate equation are (i) adsorption of O_2 on the Ag surface and (ii) reaction of gaseous CH_3OH with adsorbed O_2. The general equation, deduced elsewhere (*5*), can be written as:

$$r = \frac{k_o p_{O_2}{}^n k_m p_m{}^m}{k_o p_{O_2}{}^n + \alpha k_m p_m{}^m}, \tag{1}$$

where k_o, k_m, m, n, and α are constants. The linearized form of Eq. (1) can be written as:

$$\frac{1}{r} = \frac{1}{k_m p_m{}^m} + \frac{\alpha}{k_o p_{O_2}{}^n}. \tag{2}$$

Equation (2) implies that when $(p_m{}^m)$ is kept constant and $(p_{O_2}{}^n)$ varied or when $(p_{O_2}{}^n)$ is kept constant and $(p_m{}^m)$ varied, accordingly the plots of $1/r$ vs $1/(p_m{}^m)$ or $1/(p_{O_2}{}^n)$ should give straight lines provided the values of m and n conform to the particular mechanism under study.

In this present investigation, the values of m and n have been found to be 1 and 0.5, respectively, and $\alpha = 0.5$. So the linearized form of the equation found to obey our data, is given as

$$\frac{1}{r} = \frac{1}{k_m p_m} + \frac{1}{2k_o p_{O_2}{}^{\frac{1}{2}}} \tag{3}$$

The plots of $1/r$ vs $1/p_m$ and $1/r$ vs $1/(p_{O_2})^{1/2}$ at three different temperatures have been shown in Figs. 5 and 6, respectively. They are straight lines showing the validity of the rate Eq. (3). Finally the values of k_o and k_m have been ascertained by the usual methods and are shown in Table 2.

It may be mentioned incidentally that various authors (*4*, *5*, *16*) have found various values of m and n. They are $m = n = 1$, $m = n = 0.5$, $m = 1$, $n = 0.5$ for various studies.

For the calculation of the energies of activation, log k_o and log k_m have been plotted (Fig. 7) against $1/T$ and the values obtained are: for k_o, +22.7 kcal/mole; and for k_m, +15.0 kcal/mole.

Table 3 shows the comparison of the experimental and theoretical rates at 264°C.

The poisoning effect of H_2O has been explained by the competitive adsorption of water vapors on the catalyst surface (*18*).

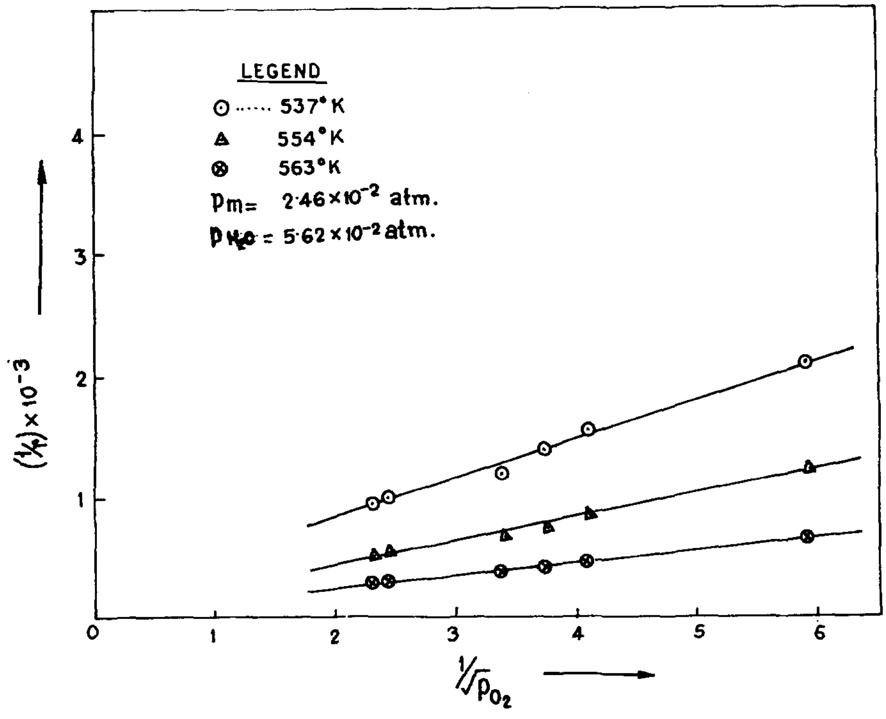


FIG. 5. Plots of $1/r$ vs $1/\sqrt{p_{O_2}}$ at various temperatures.

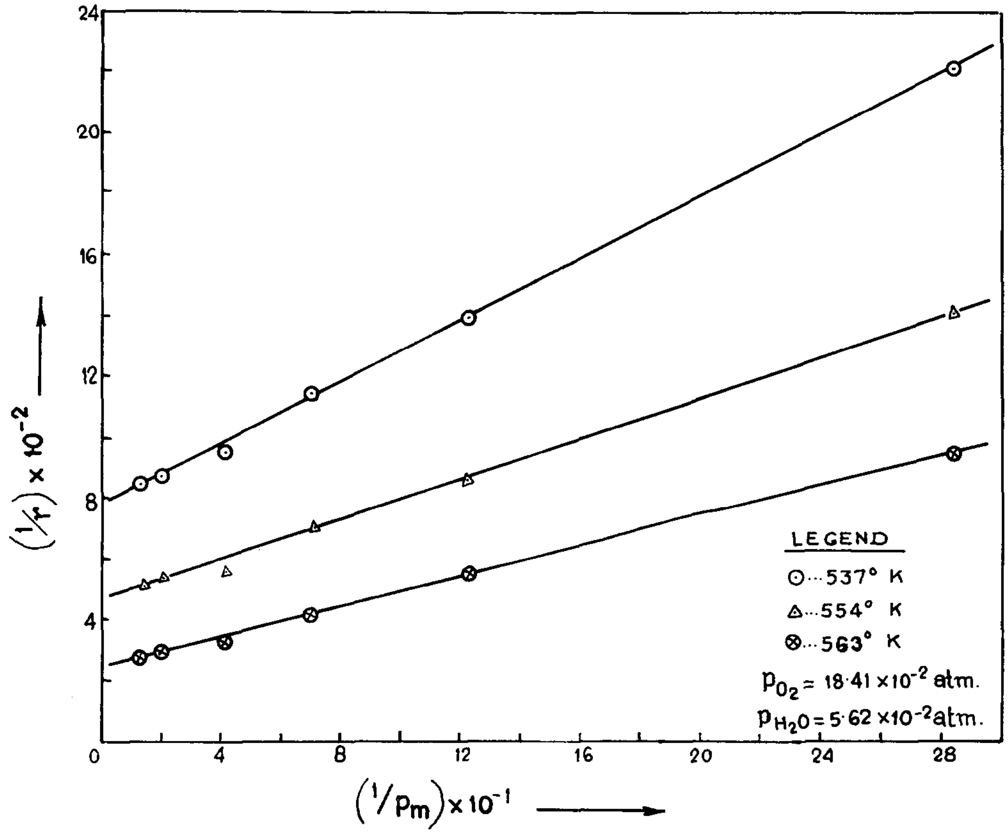


FIG. 6. Plots of $1/r$ vs $1/p_m$ at various temperatures.

From the linear variation of $1/r$, with $1/(p_{O_2})^{1/2}$, which involves the exponent 1/2 for p_{O_2}, it appears that the adsorption of O_2 is dissociative. The validity of this rate equation has also been justified by further studies. They are described below.

Equation (3) can be rewritten as

$$\left(\frac{1}{r}\right)_{p_m} = A + \frac{B}{(p_{O_2})^{\frac{1}{2}}};$$

$$\left(\frac{1}{r}\right)_{p_{O_2}} = C + \frac{D}{p_m},$$

where A, B, C, and D are constants. These two equations imply that when p_m is kept constant, the plots of $(1/r)_{p_m}$ vs $1/(p_{O_2})^{1/2}$ should give a series of parallel straight lines, all having the gradient B for different initial constant values of p_m. This also is true for the plots of $(1/r)p_{O_2}$ vs $1/p_m$ at different constant values of p_{O_2}. In practice, two sets of constant p_{O_2} and p_m values were taken as initial conditions of studies and two sets of parallel straight lines with gradients equal to B and D were found.

TABLE 2

THE VALUES OF k_o AND k_m AND ACTIVATION ENERGIES AT DIFFERENT TEMPERATURES

	Temp (°C)			Activation energies (kcal/mole)
Values	264	281	290	
k_o	1.52×10^{-3}	2.83×10^{-3}	5.00×10^{-3}	22.7
k_m	2.05×10^{-1}	2.90×10^{-1}	4.01×10^{-1}	15.0

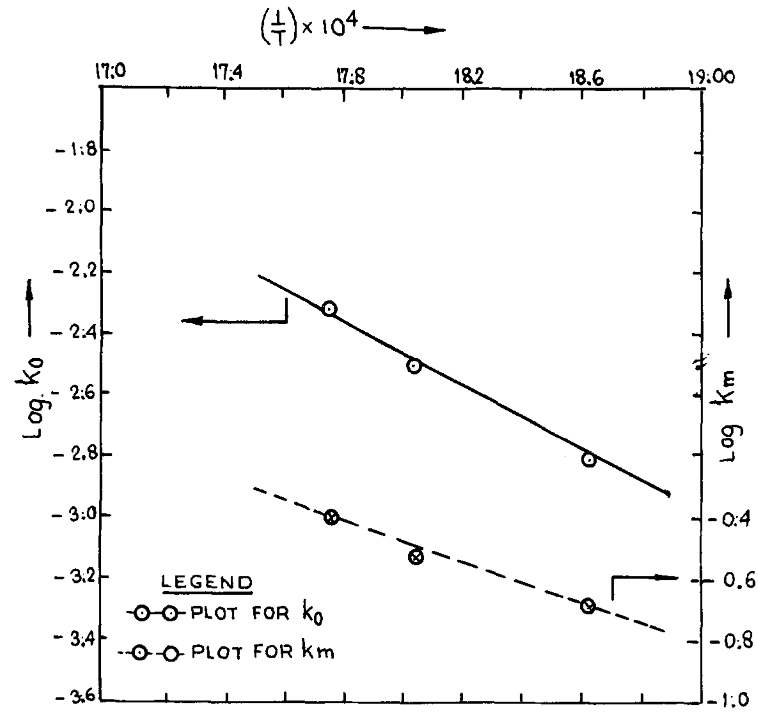


Fig. 7. Arrhenius plots.

Under the experimental conditions, a two-step cyclic operation (*19*) was performed. These are shown together with the observations below:

First cycle	Second cycle	Observations
1. O_2 swept over the catalyst	Methanol vapor (in complete absence of O_2) passed	HCHO was detected
2. Methanol (in complete absence of O_2) was swept over the catalyst	Oxygen passed	No HCHO detected

These observations indicate that while in the first case HCHO is formed, the second case does not show any HCHO. This means that in the first case, O_2 becomes adsorbed first so that this can react with CH_3OH vapor passed in the second cycle; but in the latter case, methanol is not adsorbed on the catalyst surface as a result of which no HCHO could be detected.

Regarding the state of oxygen on the catalyst surface, the rate equation predicts a dissociative adsorption, a phenomenon which has also been favored by other workers (*20, 21*).

The derivation of the rate equation and its validity being justified by experimental data, it is now worthwhile to turn to the mechanism of the process. The adsorbed oxygen may diffuse inside the lattice to bring about a change in the electronic properties of the catalyst. Some of the adsorbed oxygen may remain bound to the surface and some may become dissolved into the bulk to give a structure resembling Ag_2O (*21*). Now, it has been reported (*22*) that the bulk oxide is thermodynamically more unstable than the surface oxide, which is in conformity with Sandler's (*21*) obser-

TABLE 3

Comparison of Experimental and Theoretical Rates at 264°C

($k_o = 1.52 \times 10^{-3}$; $k_m = 2.05 \times 10^{-1}$)

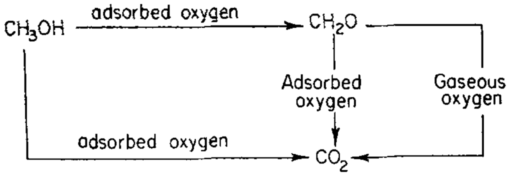
Sl. No.	$p_{O_2} \times 10^2$ (atm)	$p_m \times 10^2$ (atm)	$r \times 10^4$ Experimental	$r \times 10^4$ Theoretical
1	2.86	2.46	4.70	4.66
2	5.73	2.46	6.46	6.36
3	7.16	2.46	7.10	7.01
4	8.59	2.46	8.25	7.58
5	14.32	2.46	9.62	10.09
6	18.40	2.46	10.41	10.36
7	18.40	0.35	4.50	4.66
8	18.40	0.82	7.10	7.35
9	18.40	1.40	8.70	8.98
10	18.40	2.45	10.40	10.36
11	18.40	5.00	11.50	11.59
12	18.40	7.36	11.66	12.01

vation that even on prolonged pumping at 500°C, oxygen equivalent to 1–2.5 monolayers may remain associated with the catalyst.

So, when CH_3OH vapor comes in contact with the catalyst with adsorbed oxygen, the bulk oxide may react quickly (due to its being more unstable than the surface layer of oxygen) with it to give the products. Of course, it is very difficult at this stage to predict which portion of the adsorbed oxygen reacts with methanol.

Regarding the other product, CO_2, it is very difficult to choose between the various possible courses. One of these may be the reaction of HCHO (which is formed first) with the adsorbed oxygen on the catalyst. The gaseous methanol, when it comes into contact with the surface, may become oxidized to HCHO which in its turn, may be partly oxidized to CO_2 during its passage through the remaining portion of the catalyst bed. The second possibility is the direct oxidation of CH_3OH by adsorbed O_2 to give CO_2. The third possibility is the oxidation of CH_2O by oxygen in the gas phase. The fourth possibility of noncatalytic oxidation of CH_3OH by gaseous oxygen is ruled out due to the absence of this reaction under this specific condition.

So the tentative mechanism is given as follows:



It can be concluded that under the present experimental conditions, formaldehyde is formed by the oxidation of methanol with adsorbed oxygen, whereas CO_2 may be formed by any one of the above courses.

References

1. Thomas, M. D., *J. Amer. Chem. Soc.* **42**, 867 (1920).
2. Vlodavets, I. N., and Pshezhetskii, S. Y., *Zh. Fiz. Khim.* **25**, 612 (1951); *Chem. Abstr.* **45**, 10013 (1951).
3. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci.* **3**, 41 (1954); *Spec. Suppl. Proc. Conf. Oxid. Processes, 1954.*
4. Jiru, P., Wichterlova, B., and Tichy, J., *Proc. Int. Congr. Catal., 3rd., 1964* **1**, 199 (1965).
5. Bhattacharyya, S. K., Janakiram, K., and Ganguly, N. D., *J. Catal.* **8**, 128 (1967).
6. Shelstad, K. A., Downie, J., and Graydon, W. F., *Can. J. Chem. Eng.* **35**, 102 (1960).
7. Downie, J., Shelstad, K. A., and Graydon, W. F., *Can. J. Chem. Eng.* **39**, 201 (1961).

8. Jaswal, J. S., Mann, R. F., Juusola, J. A., and Downie, J., *Can. J. Chem. Eng.* **47**, 284 (1969).

9. Allen, J. A., *Aust. J. Chem.* **17**, 529 (1964).

10. Kolthoff, I. M., and Belcher, R., *et al.*, "Volumetric Analysis," Vol. III, p. 375. Interscience, New York, 1957.

11. Jacob, M. B., "The Analytical Chemistry of Industrial Poisons and Solvents," p. 622. Interscience, New York, 1949.

12. Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis," 3rd ed., p. 249. E. L. B. S. and Longmans, Green, 1962.

13. Jones, E., and Fowlie, R. G., *J. Appl. Chem.* 3, 206 (1953).

14. Hougen, O. A., Watson, K. M., and Ragatz, R. A., "Chemical Process Principles," Part II, Asia Publishing House, Bombay, India, 1947.

15. Corrigan, T. E., *Chem. Eng.* **62**, 199 (1955).

16. Mann, R. S., and Hahn, K. W., *J. Catal.* **15**, 329 (1969).

17. Juusola, J. A., Mann, R. F., and Downie, J., *J. Catal.* **17**, 106 (1970).

18. Pernicone, N., Lazzerini, F., Lanzavecchia, G., *J. Catal.* **10**, 83 (1968).

19. Smith, F. M., private communication.

20. Margolis, L. Ya., *Advan. Catal. Relat. Subj.* 14, 431–496 (1963).

21. Sandler, Y. L., and Hickam, W. M., *Proc. Int. Congr. Catal., 3rd 1964* 1, 227–239 (1965).

22. Gonzalez, O. D., and Parravano, G., *J. Amer. Chem. Soc.* **78**, 4533 (1956).