

## A Comparison of the Flow and Pulse Technique for the Dehydrogenation of Methanol

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The dehydrogenation of methanol to carbon monoxide has been studied by a pulse technique and in a flow reactor. The activation energy for the dehydrogenation on silver was found to be 31.3 kcal/mole by the pulse technique and 30.1 kcal/mole by the flow technique. The order of the reaction was shown in both cases to be 1.0.

### INTRODUCTION

The use of gas chromatography is now a well-established method for studying heterogeneous catalytic reactions. The two methods of operating chiefly used are the continuous-flow technique (1) and the pulse technique (2).

The former method is preferred whenever kinetic measurements are to be made, since the reactor system operates under stationary conditions and samples of this stationary mixture are analyzed in a gas chromatograph. The system can be treated theoretically by means of the Damköhler equation (3) or by similar equations such as those developed by Menold (4). A possible disadvantage of the flow reactor is the use of large quantities of reactant.

In the pulse technique the reactor is placed immediately before the chromatographic column and the carrier gas flows first through the reactor, then the column. The reactant is injected into the carrier gas stream before the reactor. Where limited amounts of reactant are available (e.g., deuterated compounds) use of the pulse technique may be unavoidable. The small quantity of reaction products involved in the pulse system is also advantageous if the reaction products are corrosive (5).

In most cases these advantages are offset by the difficulty of making kinetic measurements with the pulse technique. The system

is not in a steady state, which complicates the theoretical treatment. Thus, the pulse technique has been mostly used to investigate the product distribution or to compare a series of catalysts.

Recently an attempt was made to treat the pulse technique mathematically (6). The authors confined themselves to the case of ideal linear chromatography, in which the separation column was also the catalyst. By setting up a mass balance over a layer  $dx$  of the column, they arrive at the following equations (see the next section for the meaning of the symbols):

$$\mathfrak{C}Q \left( \frac{\partial c}{\partial t} \right)_x + Q(1 - \mathfrak{C}) \left( \frac{\partial a}{\partial t} \right)_x + \omega \left( \frac{\partial c}{\partial x} \right)_x + Q(1 - \mathfrak{C})W_p = 0 \quad (1)$$

Further, if  $W_p = ka^n$  and  $a = \Gamma c$  (i.e., equilibrium exists between adsorbed and gas phase) the equation becomes

$$\mathfrak{C}Q \left( \frac{\partial c}{\partial t} \right)_x + Q(1 - \mathfrak{C})\Gamma \left( \frac{\partial c}{\partial t} \right)_x + \omega \left( \frac{\partial c}{\partial x} \right)_x + Q(1 - \mathfrak{C})k(\Gamma c)^n = 0 \quad (2)$$

A simplification is now made by considering the ingoing pulse form to be either square-topped or triangular. For these two cases and for the values of  $n = 0, 1,$  and  $2$  the equation is solved to give the shape of the peak leaving the catalytic column.

The authors use the derived equations to investigate the kinetics of cyclohexane de-

hydrogenation to benzene and find that the results are in agreement with the equations for first order. However, a direct comparison of the results from the pulse and flow techniques was not made. Because of the many simplifications introduced, a comparison would help show the reliability of the kinetics determined by the pulse technique. To this end, the dehydrogenation of methanol on silver was studied by the pulse and flow techniques.

## NOTATION

$Q$	Cross section of reactor column (cm <sup>2</sup> )
$\mathcal{V}$	Void space of catalyst
$c$	Concentration (g/cm <sup>3</sup> )
$t$	Time (s)
$a$	Amount adsorbed (g/cm <sup>3</sup> catalyst)
$\omega$	Gas flow (cm <sup>3</sup> /sec)
$W_p$	Reaction rate (g/cm <sup>3</sup> catalyst)
$\Gamma$	Adsorption constant
$k$	Rate constant
$n$	Reaction order
$L$	Length of catalyst bed (cm)
$h$	Peak height (mm)
$h_{CO}^{\infty}$	Peak height of CO at 100% methanol conversion
$p_M^0$	Initial partial pressure of methanol (Torr)
$q$	Activation energy (kcal/mole)
$R$	Gas constant
$T$	Absolute temperature (°K)
$p$	Atmospheric pressure ( $\approx 710$ Torr)
$\alpha$	Degree of decomposition
$\tau$	Retention time over catalyst(s)
$F_M^0, F_M^e$	Initial and final area of the methanol peak
$b_{1/2}$	Width of peak at half height (mm)
$f$	Proportionality factor
$\bar{c}_M$	Mean concentration of methanol (g/cm <sup>3</sup> )
$c_M^0, c_M^e$	Initial and end concentration of methanol
$t$	Width of peak at base(s)

## EXPERIMENTAL

The methanol used was from Merck, quality "Uvasol." A gas-chromatographic

analysis showed the presence of small quantities of water and methyl formate (<1%). The silver used was foil (99.99%) from Degussa. It was dissolved in dilute nitric acid and reprecipitated with tartaric acid and sodium hydroxide solution. The silver powder was filtered off, washed, and dried.

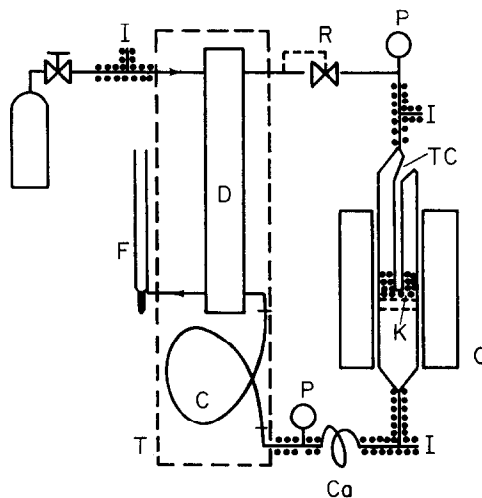


FIG. 1. Apparatus: C, chromatography column; Ca, capillary; D, detector; F, soap film flow meter; I, injection port; K, catalyst; O, oven; P, pressure gauge; R, flow regulator; T, thermostated chamber; TC, thermocouple.

A diagram of the apparatus used for the pulse technique is shown in Fig. 1. Glow plugs were used here as thermal-conductivity detectors ( $\gamma$ ). Five microliters of methanol was found to give a suitable chromatogram and unless otherwise stated this quantity was injected.

The flow apparatus is described elsewhere (8) and was used in conjunction with a Beckman GC 2 gas chromatograph with a 10-ml sampling loop.

For both methods a 4-mm diameter, 3 m long column of 20% Ethofat on Chromosorb P (acid-washed, HMDS-treated) was used. Tests had shown that with this column the possible reaction products  $H_2 + CO$ ,  $CH_3OCH_3$ ,  $CH_3OOCH$ ,  $H_2O$ , and  $CH_3OH$  are separated. As carrier gas  $H_2$  (Linde 99.996%) was used so that in the gas peak only CO was detected.

## RESULTS

For both techniques a working-in period was necessary, after which the activity remained almost constant. The slight decrease in activity over a period of days is probably due to sintering of the silver powder at the higher temperatures.

## (a) Flow Technique

The reaction was investigated on 0.55 g of powder at various flow rates and various methanol partial pressures. In all cases the chromatogram showed only two peaks—CO and CH<sub>3</sub>OH. A flow rate of 40 ml/min H<sub>2</sub> and a column temperature of 100°C was found suitable for the separation in the Beckman GC 2 chromatograph.

Since the CO peak was narrow, the peak height could be taken as proportional to the CO produced. The degree of decomposition was <1% so that the following equation was valid (8)

$$\log h_{\text{CO}} = \log k + \log L - \log \omega + n \log p_{\text{M}}^0 + \text{const.} \quad (3)$$

For constant  $L$ ,  $\omega$ ,  $n$  and  $p_{\text{M}}^0$

$$\log h_{\text{CO}} = \text{const.} - q/2.3RT \quad (4)$$

Figure 2 shows Arrhenius plots for various  $\omega$  and  $p_{\text{M}}^0$ . The values for the activation energy are given in Table 1.

TABLE 1  
ACTIVATION ENERGIES IN THE FIRST ORDER RANGE

Plot	T range (°C)	Flow rate (ml/min)	Methanol pressure (Torr)	Activation energy (kcal/mole)	Mean
<i>Flow technique</i>					
1	531-375°	34	260	25.1	} 30.1
2	528-422°	34	152	29.3	
3	531-444°	62.5	260	31.0	
4	532-445°	62.5	152	30.0	
Activation energy (kcal/mole)					
<i>Pulse technique</i>					
1	491-387°	29.2	25 ± 5	29.2	} 31.3
2	507-386°	32.0	—	32.2	
3	498-404°	31.8	—	32.2	

It can also be shown (9) that at constant  $T$ ,  $L$ ,  $\omega$ , and  $n$

$$\log [h_{\text{CO}}p/(p - p_{\text{M}}^0)] = n \log p_{\text{M}}^0 + \text{const.} \quad (5)$$

so that a plot of  $\log [h_{\text{CO}}p/(p - p_{\text{M}}^0)]$  versus  $\log p_{\text{M}}^0$  leads to a value of 1.00 for the reaction order (Fig. 3).

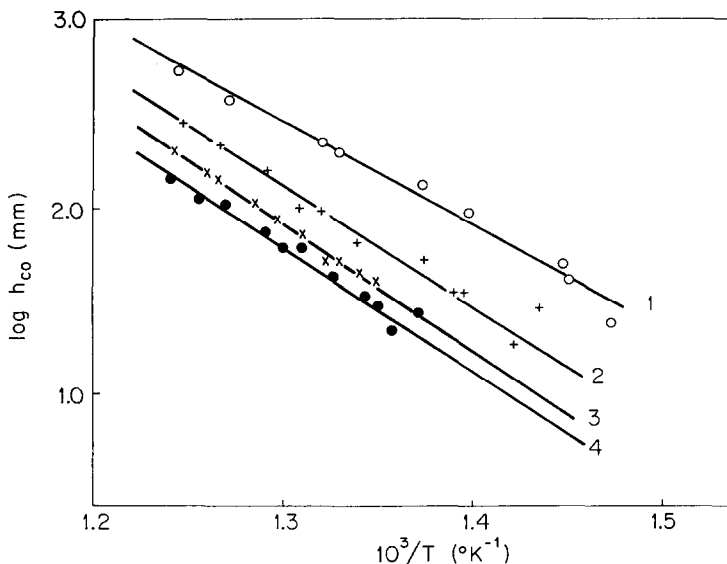


FIG. 2. Arrhenius plots for the flow technique.

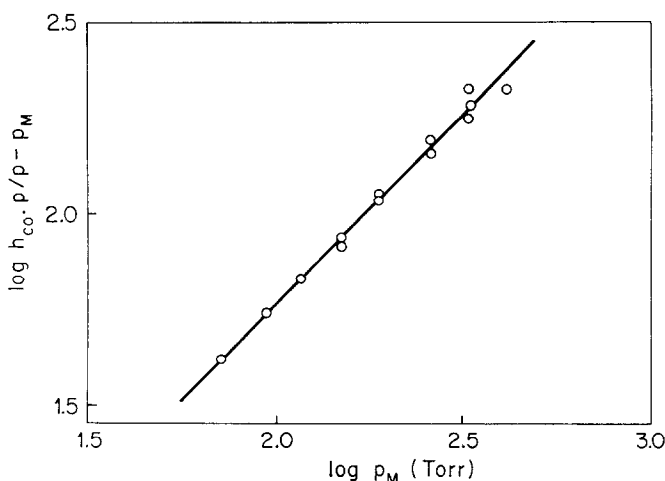


FIG. 3. Variation of corrected CO peak height with initial methanol partial pressure at 492°C and 43 ml/min H<sub>2</sub>.

#### (b) Pulse Technique

The reaction was investigated on 0.70 g of silver powder. A flow rate of 80 ml/min H<sub>2</sub> and a column temperature of 60°C was found to be satisfactory. The chromatograms show three peaks. A further analysis with a 1-m molecular sieve 5A column showed that the first peak was CO. A second small peak, which was constant throughout the whole temperature range, had an area of about 0.5% of that of the injected methanol. It was identified as methyl formate and appears to arise from the impurity in the methanol. The last peak is that of the undecomposed methanol.

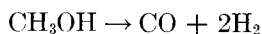
Pulse technique measurements with an inert carrier gas (He, N<sub>2</sub>) showed a peak, identified as formaldehyde, after the methanol peak. It disappeared after a few injections and apparently arises due to traces of oxide on the silver contact. The reaction products (CO and H<sub>2</sub>) reduce any oxide present so that all of the formaldehyde is finally decomposed on the contact. With H<sub>2</sub> as carrier gas the contact is already in a reduced state, so that no formaldehyde is found.

By injecting various quantities of methanol before the reference channel of the detector, the shape of the in-going peak could be determined. Even at 200°C the methanol could not be considered to vaporize instan-

taneously in the injection port, but gave a triangular-shaped peak with a little tailing. The value of  $b_{1/2}$  was about 10 sec. The flow rate of the carrier gas can thus be considered to be unaltered by the injection, since the rate of formation of methanol vapour is much smaller than the gas flow rate. Alteration of flow rate because of the formation of reaction products may also be neglected for the same reasons. The conditions of constant flow and triangular peaks may be considered as approximated.

In the case of a first order reaction the shape of the peak is reported to have no influence on the degree of decomposition (6), provided the concentration remains in the region in which the first order law is valid. This was found to be the case for the methanol dehydrogenation. Five microliter quantities of methanol were injected at various rates and the value of  $hb_{1/2}$  for CO remained approximately constant. This indicates that the reaction is indeed first order.

For a first order reaction the equations of Gaziev, Filinovskii, and Yanovskii (6) can be obtained directly. At constant gas flow, temperature, and methanol quantity the rate equation for the reaction



is given by

$$dc_{\text{CO}}/dt = -dc_{\text{M}}/dt = kc_{\text{M}} \quad (6)$$

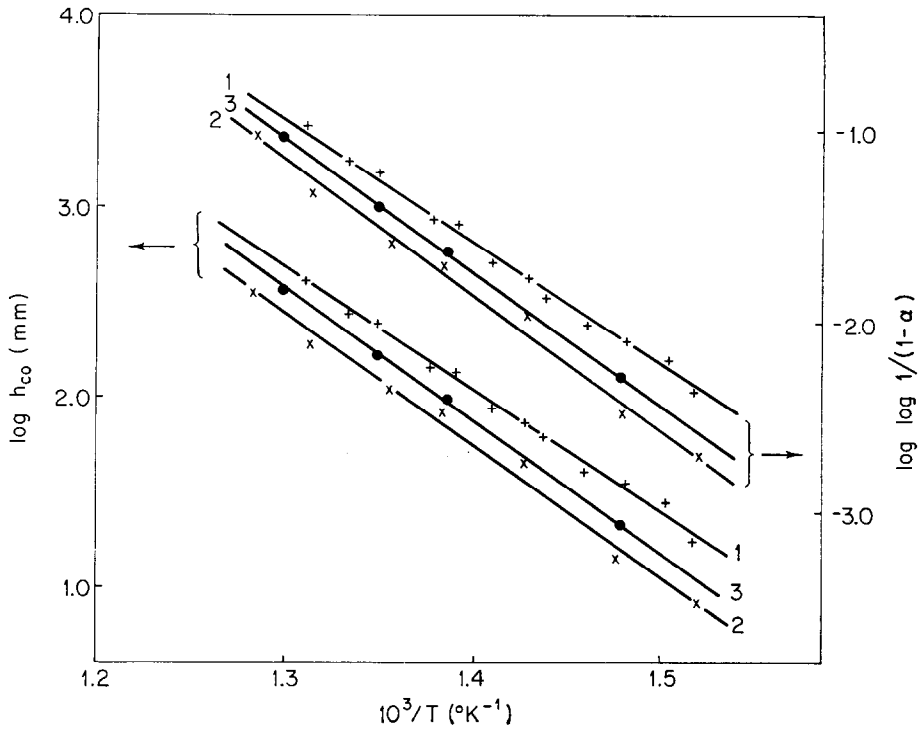


FIG. 4. Arrhenius plots for the pulse technique based on the CO produced.

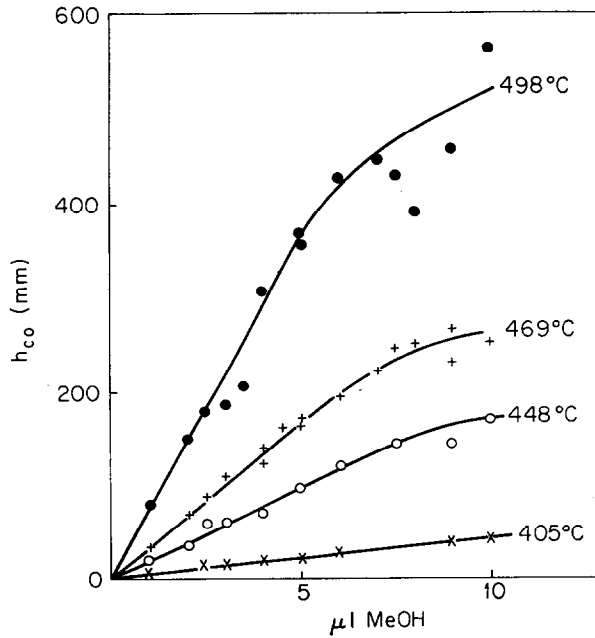


FIG. 5. Variation of CO peak height with amount of methanol injected.

The reaction time can be set equal to the contact time so

$$\ln (c_M^e/c_M^0) = -k\tau \quad (7)$$

Substituting

$$c_M^e = c_M^0(1 - \alpha) \quad (8)$$

gives

$$\ln 1/(1 - \alpha) = k\tau \quad (9)$$

The activation energy is obtained from the slope of the plot  $\log \log 1/(1 - \alpha)$  versus  $1/T$  since

$$\log \log 1/(1 - \alpha) = \text{const.} - q/2.3RT \quad (10)$$

This is the same expression derived by the above authors. It can be simplified further by considering that for  $\alpha \ll 1$

$$\ln 1/(1 - \alpha) \approx \alpha = h_{CO}/h_{CO}^\infty \quad (11)$$

so that

$$\log h_{CO} = \text{const.} - q/2.3RT \quad (12)$$

A plot of  $\log h_{CO}$  against  $1/T$  should yield a parallel to that obtained from the  $\alpha$  values, at any rate up to  $\alpha < 0.2$ .

Figure 4 shows plots of Eqs. (10) and (12). The good agreement indicates that the assumption of first order is justified. Each point is a mean of four or five measurements. The  $h_{CO}^\infty$  value was obtained from a separate calibration with CO.

The fact that the degree of reaction is independent of the amount of reactant for the first order can also be used to confirm the assumption of first order. One to 10  $\mu$ l quantities of methanol were injected and  $h_{CO}$  plotted against  $\mu$ l of methanol, as in Fig. 5. The straight lines obtained show that the first order relationship

$$h_{CO} \sim c_{CO} = c_M^0 - c_M^e = c_M^0(1 - e^{-k\tau})$$

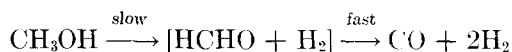
holds. In this case  $\overline{c_M^0} t$  instead of  $c_M^0$  is more appropriate, since the former gives the amount of methanol, independent of the peak shape.

The scattering of the measured points at larger quantities of methanol is probably due to disturbances in the flow, temperature, etc., at the higher degrees of decomposition.

The results for both techniques are given in Table 1.

## DISCUSSION

The results from both techniques are in good agreement for the reaction order as well as the activation energy. In addition the values compare favorably with a value of 30.8 kcal/mole reported for the dehydrogenation of methanol over alumina-supported silver (10). Since the measurements with He and N<sub>2</sub> carrier gas indicate the formation of formaldehyde as intermediate, it is likely that formaldehyde is also formed with H<sub>2</sub> as carrier gas. The measured activation energy is considered to be that of the first stage of the reaction



Menold (11) also considers a two-stage mechanism for the dehydrogenation on zinc oxide.

It is also possible to form the  $\alpha$  values from the amount of methanol decomposed, since

$$c_M^0 = fF_M^0 \quad (13)$$

and

$$c_M^e = fF_M^e = c_M^0(1 - \alpha) \quad (14)$$

so that

$$\begin{aligned} \log \log 1/(1 - \alpha) &= \log \log F_M^0/F_M^e \\ &= \text{const.} - q/2.3RT \quad (15) \end{aligned}$$

The values of  $\alpha$  so formed are not as exact as those from  $\alpha = h_{CO}/h_{CO}^\infty$ , especially at low degrees of conversion, where the values of  $F_M^0$  and  $F_M^e$  are almost equal. Figure 6, curve a, shows a plot of Eq. (15) in which the peak height has been taken as proportional to  $c_M$ . The value of  $q$  obtained is not in agreement with the value from  $\alpha_{CO}$ . Setting  $hb_{1/2} \sim c_M$  does not greatly alter the plot. Only when the methanol curves are integrated with a planimeter is the activation energy approximately the same as obtained with  $\alpha_{CO}$  (Fig. 6, curve b).

The explanation for the above is that the tailing of the methanol peak is not accounted for in forming  $hb_{1/2}$  (or  $h$ ). The tailing of the  $c_M^e$  peak is slightly increased by the silver contact, so that a comparison with the  $c_M^0$  peak, in which the tailing is not so large, leads to a false value for  $1/(1 - \alpha)$ . By integrating the peaks and by

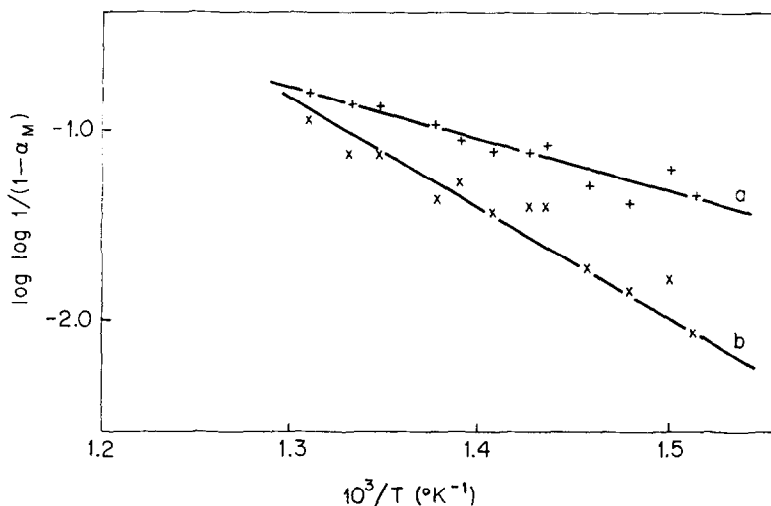


Fig. 6. Arrhenius plots for the pulse technique based on the methanol consumed.

calibrating  $c_M^0$  between each point measured (i.e., injecting 5  $\mu$ l of methanol behind the silver contact), to minimize alterations in the ratio  $F_M^0/F_M^e$  caused by small fluctuations in temperature, gas flow, and filament current, the  $\alpha$  values become more reliable but the points still show a wide scattering around the Arrhenius plot in Fig. 6(b).

Finally, after use, the reactor is slightly discolored, suggesting that a small fraction of the injected methanol has been "cracked." The "disappearance" of methanol results in  $\alpha$  values which are too large. The amount of coking, however, is so small that only at the smallest degrees of conversion could it alter  $\alpha$  noticeably. At larger degrees of decomposition the  $\alpha_M$  values are about the same as the  $\alpha_{CO}$  values.

In conclusion, it would appear that for a simple first order reaction, the pulse technique, if operated with due care, can lead to the same kinetic data as obtained with a flow system.

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