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PYROLYSIS OF FORMALDEHYDE

BY

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A THESIS

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ABSTRACT

The thermal decomposition of pure formaldehyde was studied over the temperature range of 516.6° to 466.3°C and over a pressure range of 50.0 to 162.0 Torr. The orders of carbon monoxide, hydrogen and estimated methanol formation with respect to formaldehyde concentration were found to be 1.8, 1.6 and 2.0 respectively. The rate constants of carbon monoxide, hydrogen and estimated methanol production at this temperature and pressure range was measured.

A mechanism was also proposed which was consistent with the experimental results.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. D. J. McKenney for his encouragement, guidance and assistance throughout the course of this work.

I would also like to thank Dr. S. J. Price for numerous assistances and discussions.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

In spite of the fact that formaldehyde is an important intermediate in several gas phase reactions of oxygen-containing low molecular weight compounds (1,2), the mechanism of the formaldehyde pyrolysis is still not well established. There are significant discrepancies, particularly in the activation energy of the overall reaction and the nature of the individual steps postulated by different investigators.

Fletcher (3) studied the thermal decomposition of pure formaldehyde at 510° to 607°C by means of manometric measurements. He interpreted his results in terms of a second-order rate law. The yield of carbon monoxide was higher than of hydrogen. The difference between carbon monoxide and hydrogen was suggested to be due to a molecular reaction producing methanol and carbon monoxide. The methanol subsequently slowly decomposes into carbon monoxide and hydrogen. His overall activation energy for this reaction was 44.5 kcal.

In 1955, Longfield and Walters (4) pyrolysed pure formaldehyde in the temperature range of 393° to 458°C and over an initial pressure range of 110 to 240 Torr. They observed that the rate of the reaction increased only slightly for a 35-fold increase in the surface to volume ratio.

For the reaction producing methanol and carbon monoxide, they assumed that the amount of formaldehyde disappearing was equal to twice the methanol formed. The reaction order obtained on this assumption was equal to 1.7. Their activation energy for this reaction was about 31 kcal/mole and the A factor was approximately $0.9 \times 10^8 T^{\frac{1}{2}}$ liters/mole min.

Evidence suggesting that the decomposition is primarily a free radical chain reaction comes from the work of Kodama and Takezaki (1952) (5) and Longfield and Walters (1955) (4). These authors showed that methyl radicals from the pyrolysis of azomethane induced a radical chain decomposition in formaldehyde. Conclusive evidence came in 1956 from the work of Klein et al (6) who pyrolyzed formaldehyde and formaldehyde-d_2 mixtures and observed isotopic scrambling. They did not establish any kinetic parameters however, and second-order reactions were assumed for hydrogen and carbon monoxide formation based on Fletcher's (3) earlier interpretation. Methanol yields were assumed to be given by the difference between carbon monoxide and hydrogen yields and therefore also assumed to follow second-order kinetics. The reaction rate was independent of the surface to volume ratio in a baked vessel, but sensitive to the treatment of the vessel.

More recently, in 1965, Gay et al (7) pyrolyzed formaldehyde over the temperature range of 1400° to 2100°K in a shock tube. They found the rate of formaldehyde decomposition to be first order with respect to formaldehyde and first order with respect to inert (carrier) gas. They also observed a short induction period and isotopic scrambling. Methoxyl (CH_3O) radicals were detected mass spectrometrically. Their experimental rate constant is given by,

$$\log_{10}k = (12.67 \pm 0.30) - \left[(27770 \pm 2540)/4.58T\right]$$

Gay et al (7) considered a number of possible mechanisms including the following simplified Rice-Herzfeld (8) scheme;

$$CH_2O + M \longrightarrow CHO + H + M \qquad [1]$$

$$H + CH_2O \longrightarrow H_2 + CHO \qquad [2]$$

$$CHO + M \longrightarrow H + CO + M \qquad [3]$$

$$CHO + H \longrightarrow H_2 + CO \qquad [4]$$

Where M represents a third body.

The overall activation energy predicted by this mechanism was estimated to be about 60 kcal which is too high to accept, even though the predicted second-order rate law holds. They therefore proposed two alternative mechanisms which would lead to closer agreement with the observations.

Mechanism I

$$2CH_2O \longrightarrow 2\ CHO + H_2 \qquad [5]$$

$$CHO + M \longrightarrow H + CO + M \qquad [3]$$

$$H + CH_2O \longrightarrow CO + H_2 + H \qquad [6]$$

$$H + CHO \longrightarrow H_2 + CO \qquad [7]$$

Mechanism II

$$2\ CH_2O \longrightarrow H_2COH + CHO \qquad [8]$$

$$CHO + M \longrightarrow H + CO + M \qquad [3]$$

$$H_2COH + M \longrightarrow H_2 + CHO + M \qquad [9]$$

$$H + CH_2O \longrightarrow H_2 + CHO \qquad [2]$$

$$2\ CHO \longrightarrow 2\ CO + H_2$$

$$(\text{ or } CH_2O + CO) \qquad [10]$$

Both of these mechanisms predict a second-order rate law and a lower overall activation energy. They estimated the overall activation energy as 27 kcal and 48 kcal for mechanism I and mechanism II respectively. Mechanism I however does not explain the formation of the methoxyl radical and also includes an unusual initiation step. On this basis mechanism II appears to be more reasonable but not entirely adequate.

In summary, a survey of the relatively few studies of the pyrolysis of formaldehyde that have been made reveals serious discrepancies in observations and conclusions. This work was undertaken with the intention of resolving some of these questions.

EXPERIMENTAL

Apparatus.

This experiment was carried out in a conventional static vacuum system. A removable section was incorporated for formaldehyde generation and purification. The entire system could be evacuated to a pressure of 5×10^{-6} Torr by means of a three stage mercury diffusion pump , and a Welch "Duo Seal" model 1400 oil vacuum pump. After completion of about 40 runs , the entire system was heated with a yellow flame to remove formaldehyde polymer which slowly collected on the inner walls. A schematic diagram of the system is shown in Figure 1.

The removable section for the generation and purification of formaldehyde was a modification of the apparatus used by Spence and Wild (9). It could be periodically removed and cleaned with concentrated nitric acid.

The reaction vessel was a 277 cc quartz cylinder. The volume of the connecting tubing amounted to a reactor dead space of less than 2%.

The Furnace.

The reactions were carried out in a furnace consisting of a 5" diameter steel block. The steel block was 12" long with a 2¼ hole bored axially down the center to

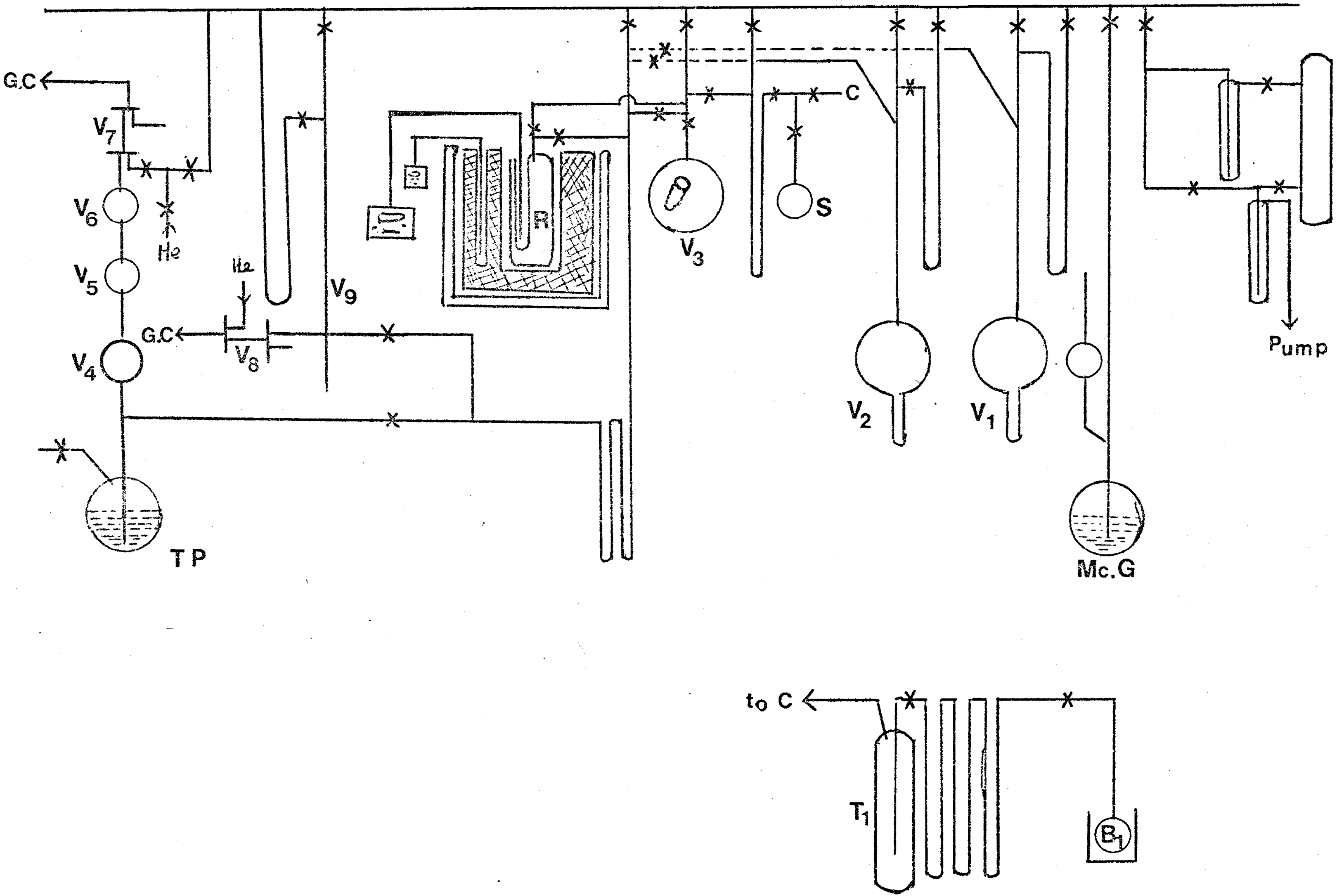

Fig. 1 Schematic Diagram of the Apparatus

a depth of approximately 10". About 1 5/8" off the central axis a 3/8" diameter hole was bored to allow for insertion of a resistance thermometer. The depth of this hole was approximately 8". The cylindrical heating chamber was nickel plated. It was wound with two coils of approximately 22 feet each of Chromel A wire ribbon, having cross-sectional area of 5/32 in^2 and a resistance of 0.606 ohms per foot. The second coil was wound around the cement coated oven. The oven was then lowered into a can insulated with Alumina. This second coil was not utilized for the experiments described in this work. The overall coil resistance was about 13 ohms. The heating unit was designed for a maximum power output without excess overloading. Using an input voltage of approximately 120 volts, the output of the furnace was about 1000 watts.

Storage Vessels and Calibrated Volumes.

The vacuum system used contained two large (approximately 2-liter) vessels, V_1 and V_2 for future storing of the inert gas (carbon dioxide) and formaldehyde respectively. Each vessel had a five inch cold finger. The system also contained a one-liter mixing vessel, V_3 , equipped with a cold finger.

Above the Toepler pump, TP , was a gas burette consisting of three water calibrated bulbs, V_4, V_5 , V_6 of

101.83 cc, 39.46 cc and 24.98 cc capacity respectively. The injection chamber, V_7 , was a 6.10 cc tubing connected to the upper column of a gas phase chromatograph for analyzing the permanent gases. Another injection chamber, V_8 , with a volume of 2.57 cc was connected to the lower column of the gas phase chromatograph for analyzing aliquots of the condensible gases. A volume of 83.43 cc, V_9 , was also used as storage of condensible gases.

Pressure Measurements.

The pressure of the system was measured by a McLoed gauge. The pressure of formaldehyde in storage vessel(V_2) was measured by a constant volume mercury manometer. This manometer was usually kept isolated from the rest of the system and only opened briefly for the required pressure measurements. The total pressure of non-condensible gases was measured by the difference of mercury level in the gas burette and the side arm of Toepler pump. Readings were taken using a cathetometer.

Temperature Measurements.

The temperature of the furnace was controlled to within $\pm 0.25^{\circ}C$ with a Sunvic type RT_2 proportional controller in conjunction with a platinum resistance thermometer. The temperature of the reaction vessel was monitored using a chromel-alumel thermocouple and Leeds and Northrup model 8691 millvolt potentiometer. The temperature of Glas-col was measured with a chromel-alumel thermocouple and controlled by means of a variac. The reference junctions of the thermocouples were immersed in a distilled water-ice slush bath.

Analytical System.

A full description of the procedure and coolants used appears in the experimental procedure.

The reactant and products were separated by expansion through a double-U tube trap immediately following the reaction vessel. Non-condensible gases were transferred and collected by means of a Toepler pump.

The system shown in Figure 1 was connected directly to a F & M model 700 gas chromatograph. Aliquots of the condensible gases were quantitatively analysed on a copper, six foot, one quarter inch, 80/120 mesh polypak column at 90 ± 0.5°C. The non-condensible gases were analysed on a copper, six foot , one quarter inch, 45/60 mesh molecular sieve 5 A column at 90 ± 0.5°C. A thermal conductivity detector was used and maintained at a temperature of 140°C. The filament current was maintained at 150 mA. Helium at 30 pounds per sqare inch pressure and at a flow rate of about 76 cc per minute in both upper and lower columns was used as a carrier gas

Preparations of Formaldehyde.

Formaldehyde was first prepared using Jost's (10) method. According to this method, paraformaldehyde was mixed thoroughly with phosphorus pentoxide in the decomposition bulb (B_1) as shown in Figure 1. The air in the bulb was then pumped off by connecting the bulb to the vacuum system. The paraformaldehyde was decomposed under vacuum within the temperature range from 60° to 90°C . The formaldehyde gas was collected in a liquid nitrogen trap. The chromatogram of formaldehyde sample prepared in this way indicated the presence of an impurity tentatively assigned to methanol. The impurity could not be removed by up to six vacuum distillations.

A modification of the method developed by Spence and Wild (9) was therefore employed. This involved the direct decomposition of paraformaldehyde under vacuum. The paraformaldehyde "Fisher Purified" was dried in a vacuum desiccator over concentrated sulphuric acid for two days before being placed in the decomposition bulb (B_1). The preparation section was pumped off by a mercury diffusion pump and at the same time heated with a yellow flame. It was then isolated by closing the stop cock leading to the main line and heated again while a small amount of formaldehyde was produced by heating bulb (B_1) . This procedure minimized the troublesome formaldehyde polymerization on the surface. Polymerization is known (9) to be enhanced by adsorbed oxygen and water vapour. The system was then pumped and isolated. The purification section consisted of double-U tubes which were immersed in a dryice-acetone cooling bath and a trap (T_1) cooled in liquid nitrogen. The rate of decomposition of the paraformaldehyde was controlled by rough adjustment of the temperature between 90° to 120°C.

After the paraformaldehyde was consumed to about one fourth of initial amount, the remainder gradually became light brown in colour. The distillation was stopped at this stage.

Liquid formaldehyde collected in trap (T_1) slowly polymerized to a white solid which could be eliminated by further distillation. After six distillations through the double-U tubes at dry-ice temperature, the liquid formaldehyde was quite stable and could be stored at liquid nitrogen temperature without polymerization. In practice, The periodic warming of the trap required to take samples for reaction resulted in some polymerization.

The formaldehyde prepared by this above method was periodically analyzed by gas phase chromatography. Only one peak, that corresponding to formaldehyde, was observed at the highest sensitivity. Methanol can be detected by a gas chromatograph at this highest sensitivity range to 0.02 to 0.05 % presence in formaldehyde.

Conditioning of the reaction vessel.

The reaction vessel was conditioned by washing twice with hot (about 80°C) concentrated nitric acid and then put back into the furnace. It was then evacuated using first the mechanical pump, then the mercury diffusion pump for several hours. Results from a few of the initial runs in a series usually tended to be scattered. Discrepancies decreased with each successive run and after three or four trials the results became fully reproducible. When the reaction vessel was unused for periods of more than three hours it was always reconditioned by a run of about one minute's duration.

Experimental Procedure.

A preliminary treatment of the entire system except for the main line was carried out by evaporating a small amount of formaldehyde to about 2 Torr and heating with a yellow flame for about one minute. The system was then evacuated while continuing the heat treatment.

The formaldehyde was slowly evaporated into the storage vessel (V_2) from storage vessel (S) by removing the liquid nitrogen bath. The rate of evaporation was controlled by occasionally cooling with a dryice-acetone bath. The stop cock was closed when the desired pressure was reached and the storage vessel (S) was immediately immersed into a liquid nitrogen bath. After the formaldehyde was expanded into the reaction vessel, the cool finger under the storage vessel (V_2) was immersed into the nitrogen bath and the stop cock connecting the manometer was closed. This minimized polymerization in the stop cock bore and in the glass tubing.

The initial amount of formaldehyde in the reaction vessel was calculated by the pressure indicated on the manometer connected to V_2 .

The reaction times were varied from 6 seconds to 120 seconds depending on the reaction rate. Most of the reaction rates were determined by six runs. After each run the reactant and products were expanded from the reaction vessel through a double-U trap maintained at liquid nitrogen temperature. All the condensible gases, formaldehyde and methanol remained in the trap. The non-condensible gases consisting of hydrogen and carbon monoxide were collected in the gas burette (consisting of V_4 , V_5 , V_6) by means of the Toepler pump, TP . The total pressure of permanent gases was measured using a cathetometer. The condensible gases in the double-U trap were transferred to a storage (V_9) and then expanded into a 2 cc injection chamber. The aliquot of formaldehyde in the injection chamber was analyzed chromatographically on a polypak column at 90°C . The inlet pressure and flow rate of carrier gas were always maintained at 30 pounds per square inch and 76 cc per minute respectively. Carbon monoxide was analyzed on a molecular sieve 5A column at 90°C. Hydrogen was calculated by difference from pressure measurement of the gas burette. Both formaldehyde and carbon monoxide were measured from the peak heights of the chromatogram. The entire system was then evacuated to a pressure less then 10^{-5} Torr and pumped at least 30 minutes before the next run.

The reactions were carried out over a temperature range of 466° to 516°C.

Errors.

The cooling effect involved upon addition of reactant to the reactor was insignificant.

A check over the entire length of the reaction vessel indicated that there was no noticeable temperature gradient. The oven temperature of the gas chromatograph was strictly controlled to within ±0.5°C. Within these temperature limits the peak height variation for a fixed quantity of carbon monoxide was less than 1% corresponding to an error in carbon monoxide analyses of approximately 1%. Readings of initial formaldehyde pressures contained an estimated error of ± 0.5 mm due to the polymerization of traces of formaldehyde gas. Pressure reading of the gas burette was estimated to be about ± 0.2 mm. This accounts for a total error in carbon monoxide analyses of about 3%. Since the hydrogen yields are calculated by difference from pressure measurements, the estimated accumulated error could be as large as 10%.

RESULTS

The pyrolysis of pure formaldehyde was studied in this work over the temperature range of 466° to 516°C and over a pressure range of 50 to 162 Torr. These ranges were chosen since the rates are conveniently measured under these conditions and polymerization processes are minimized providing the formaldehyde is sufficiently purified (4,6. 9,11).

Carbon Monoxide.

The reaction times are supposed to be short enough that all experiments are carried out in the low conversion stage ($< 5\%$) of the reactions. Typical plots of carbon monoxide yield at five different initial pressures against time at 516°C are shown in Fig.2 . Since the plots all show fairly good linearity, the slopes can be considered to represent the initial reaction rates of carbon monoxide formation without significant error. The results are listed in Table 1 (page 19). Fig. 3 shbws a double logarithmic plot of initial rate of carbon monoxide formation versus formaldehyde concentration. The order of carbon monoxide formation with respect to formaldehyde concentration can be seen in Fig. 3 to be 1.8 slightly different from the results of all former investigators who assumed a second-order dependence.

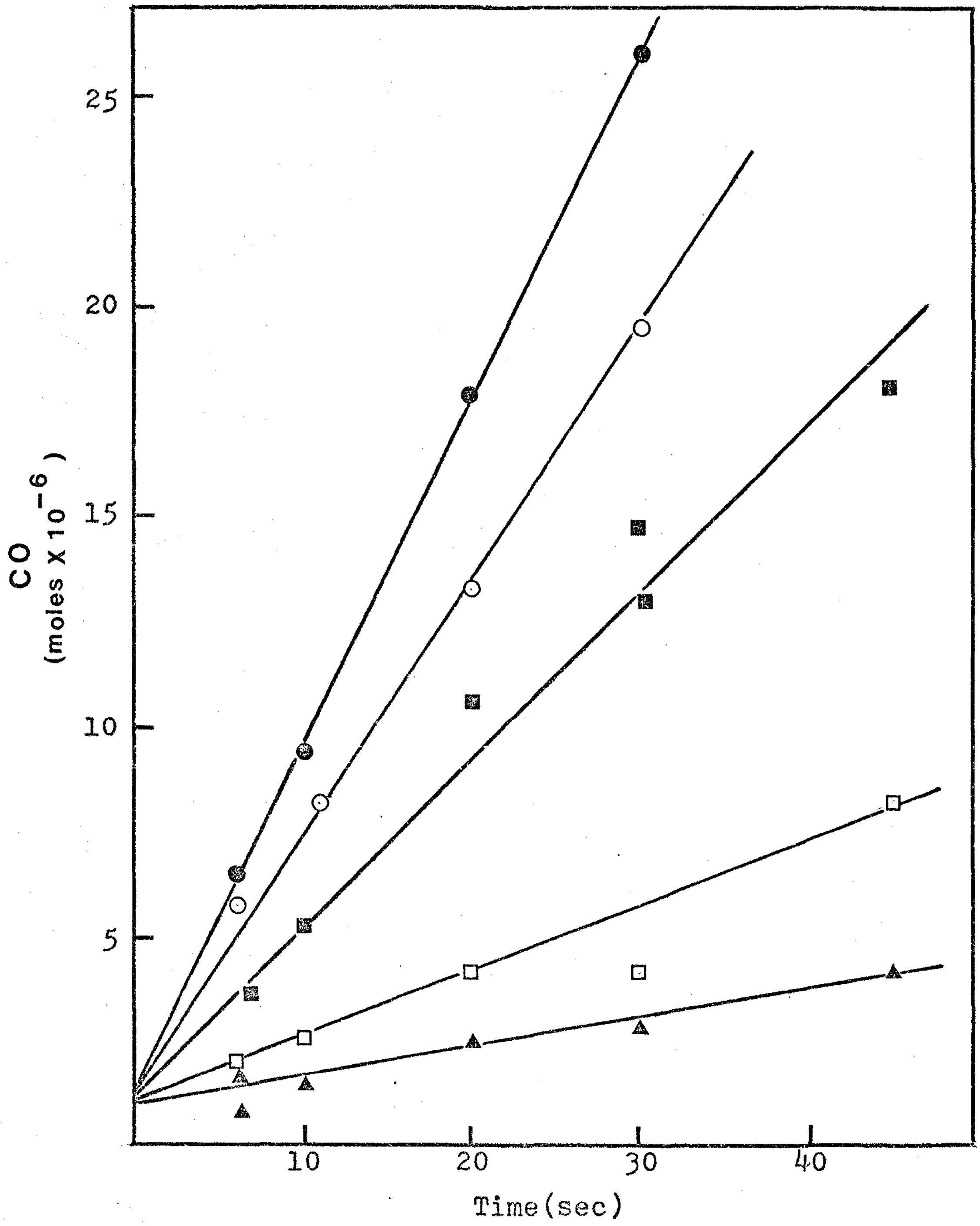

Fig. 2: Yield-time plot for carbon monoxide at 516.6°C over five different formaldehyde pressure;

● 162.0 mm ; ○ 143.5 mm ; ■ 115.0 mm

□ 71.0 mm ; ▲ 50.0 mm.

TABLE 1
INITIAL RATES OF CARBON MONOXIDE AND HYDROGEN

P(CH_2O) (mm)	Temp (°C)	R(CO) (moles x 10^{-9} cc^{-1} sec^{-1})	logR(CO)	R(H_2) (moles x 10^{-9} cc^{-1} sec^{-1})	logR(H_2)
162.0	516.6	2.58	-8.588	1.26	-8.898
143.5	516.6	2.20	-8.657	1.01	-8.996
115.0	516.6	1.56	-8.807	0.721	-9.142
71.0	516.6	0.560	-9.251	0.317	-9.499
50.0	516.6	0.356	-9.449	0.184	-9.735
162.0	500.0	1.75	-8.758	0.959	-9.018
143.5	500.0	1.37	-8.862	0.746	-9.127
115.0	500.0	0.755	-9.122	0.368	-9.434
71.0	500.0	0.382	-9.418	0.231	-9.637
50.0	500.0	0.221	-9.675	0.136	-9.868
162.0	483.2	1.22	-8.915	0.629	-9.301
143.5	483.2	1.06	-8.973	0.465	-9.333
115.0	483.2	0.541	-9.267	0.281	-9.551
71.0	483.2	0.231	-9.636	0.126	-9.899
50.0	483.2	0.132	-9.879	0.0851	-10.070
162.0	466.3	0.720	-9.143	0.264	-9.578
143.5	466.3	0.609	-9.215	0.223	-9.651
115.0	466.3	0.411	-9.386	0.150	-9.811
71.0	466.3	0.168	-9.775	0.122	-9.948

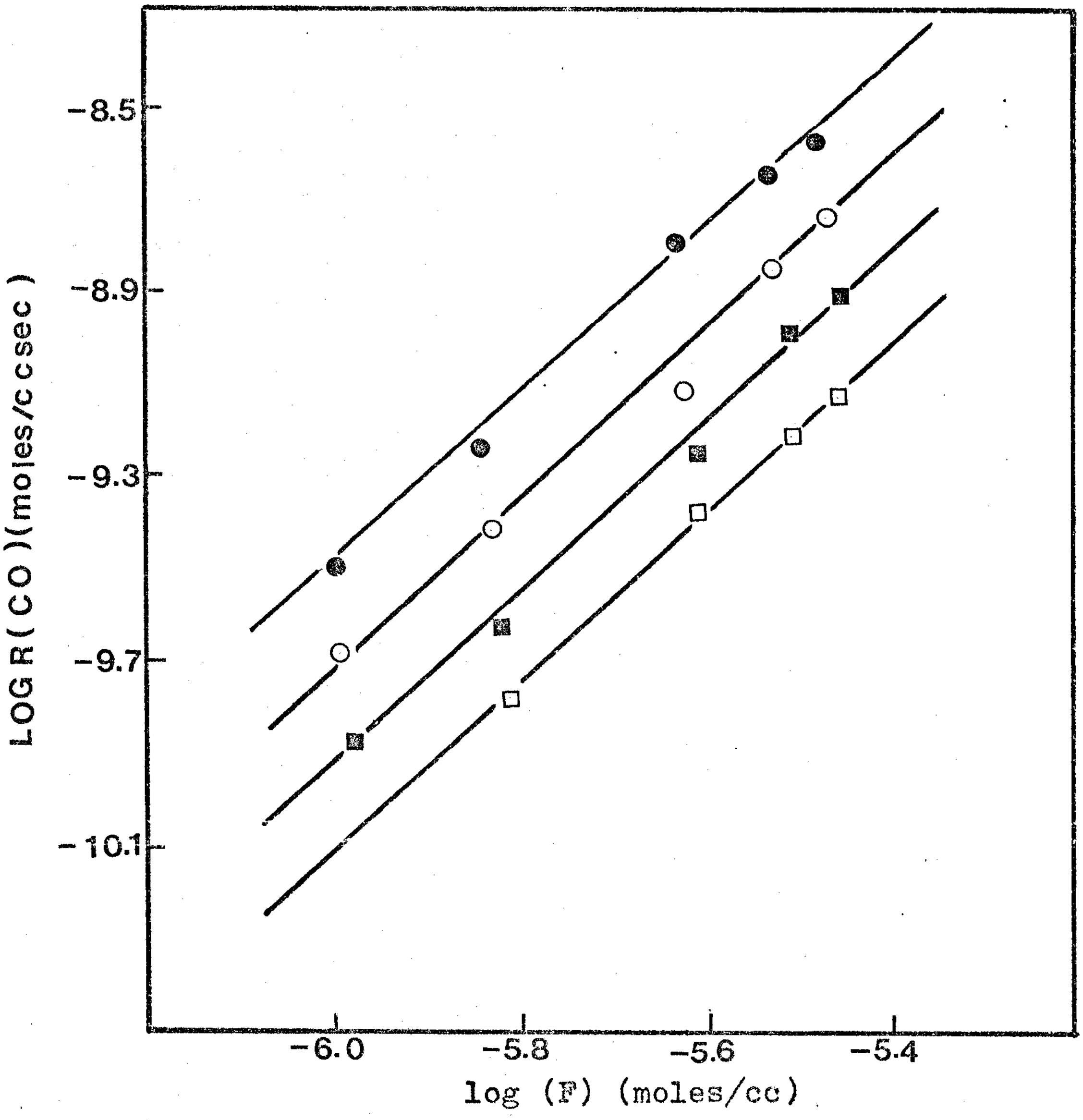

Fig. 3: Log rate of carbon monoxide production against log formaldehyde concentration at

● 516.6°C

○ 500.0°C

▨ 483.2°C

□ 466.3°C

The slopes are all 1.8 .

An Arrhenius plot of carbon monoxide formation as shown in Fig. 4 leads to an A factor of about 11.78±0.4 $cc^{0.8}/mole^{0.8}$ sec and an activation energy of 34.4±1.3 kcal/mole. This value of activation energy is much lower than the 44.5 kcal/mole obtained by Fletcher (3) for the overall reaction.

Hydrogen.

Hydrogen is the second major product in the gas phase pyrolysis of pure formaldehyde. The hydrogen yield-time plot at 516°C at five different initial formaldehyde pressures are shown in Fig. 5. The data are much more scattered then in carbon monoxide case as a result of the combined errors involved in the carbon monoxide analysis and the manometer readings. The initial rates of hydrogen production are shown in Table 1. The plots of log rate of hydrogen formation against log concentration of formaldehyde as shown in Fig. 6 leads to approximately three-half order dependence with respect to formaldehyde concentration. The activation energy and A factor obtained from the Arrhenius plot in Fig. 7 are estimated as 34.0±3.6 kcal/mole and 9.60 ± 1.0 $cc^{0.5}/mole$ sec respectively. The uncertainty in these values are estimates of the maximum probable error.

Methanol.

A quantitative analysis of the low yields ($< 10^{-8}$ mole/cc) of

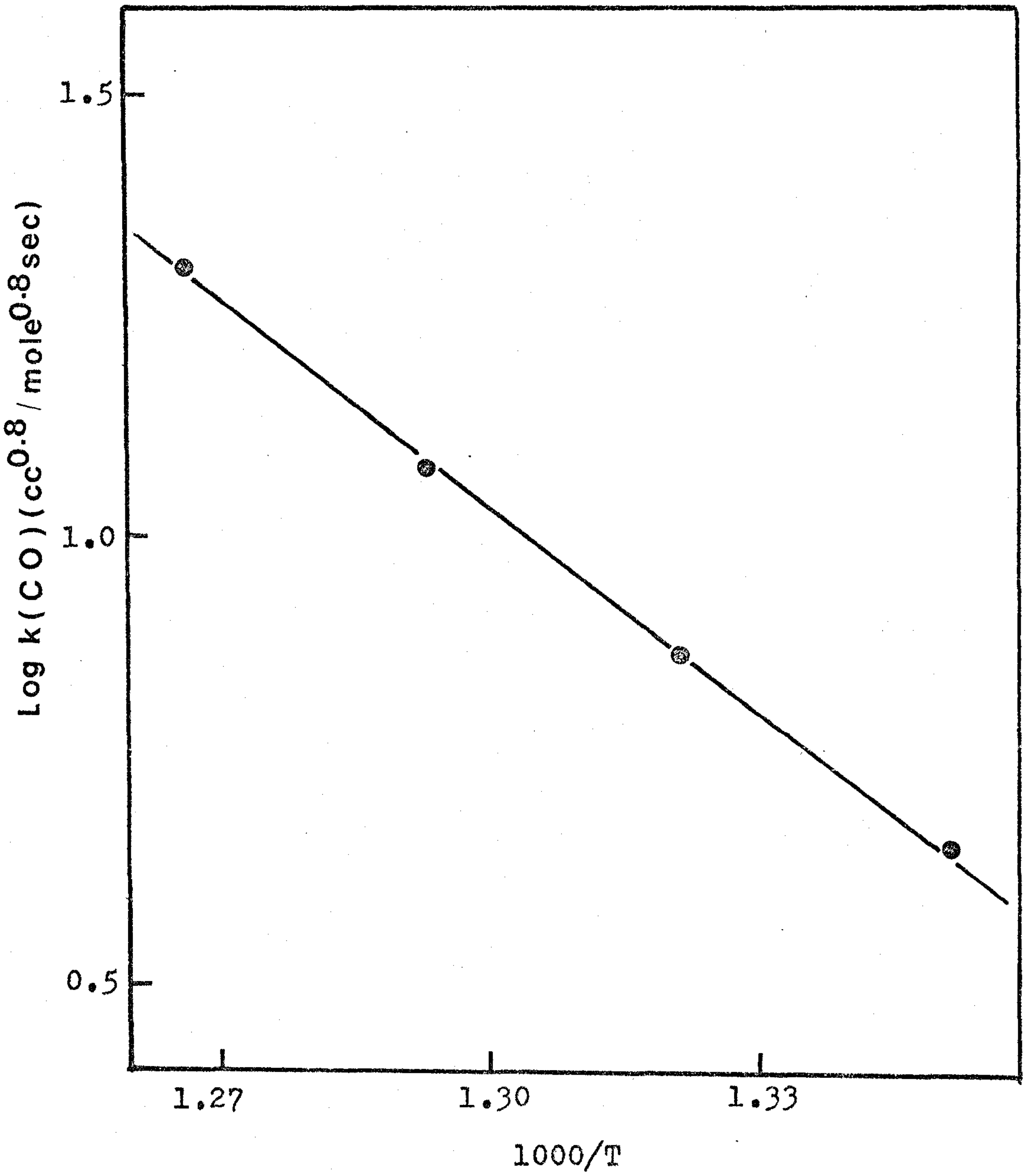

Fig. 4: Arrhenius plot of the rate constants of carbon monoxide production.

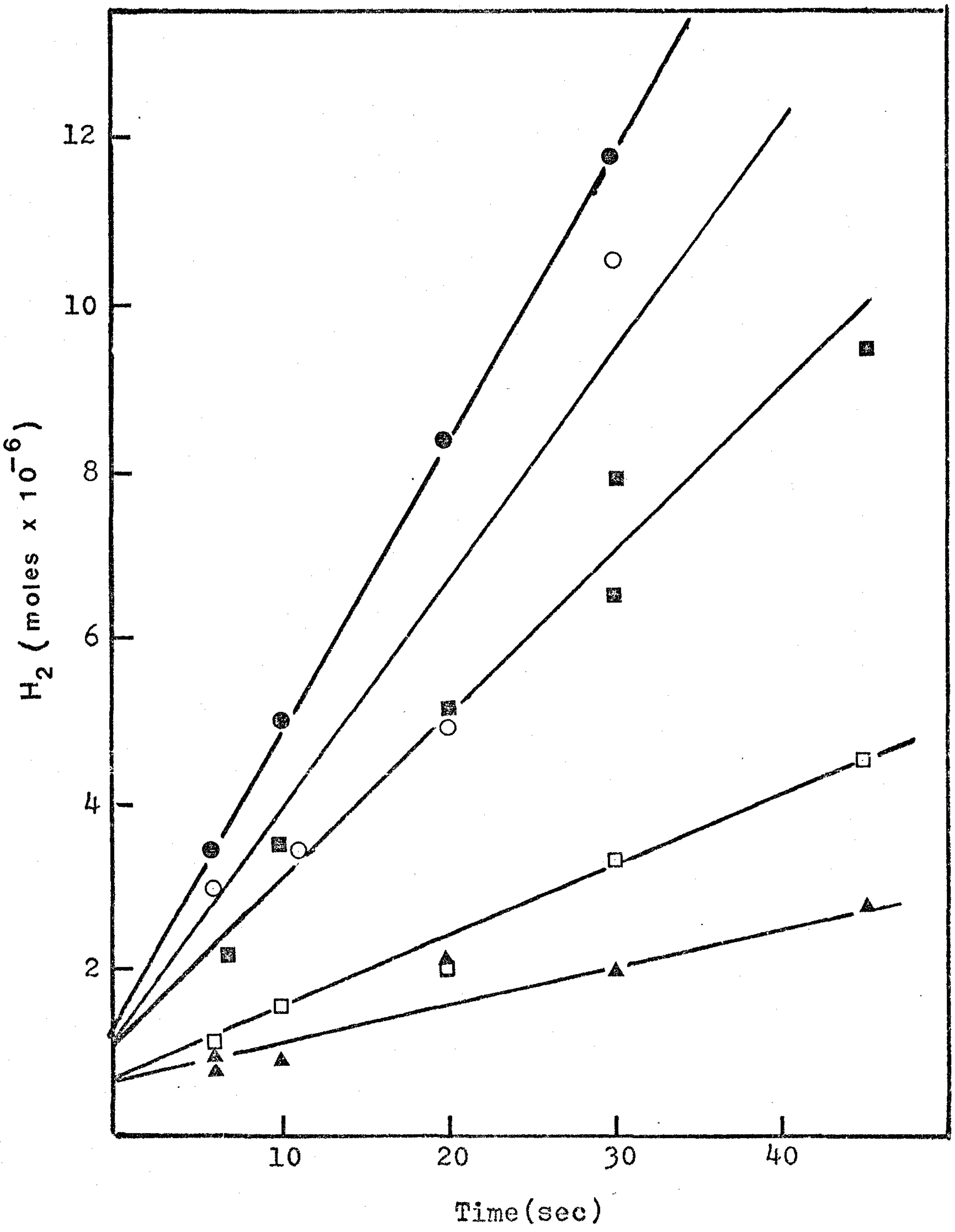

Fig. 5: Yield-time plot for hydrogen at 516°C over five different formaldehyde pressures; ● 162.0 mm; ○ 143.5 mm; ■ 115.0 mm; □ 71.0 mm; ▲ 50.0 mm.

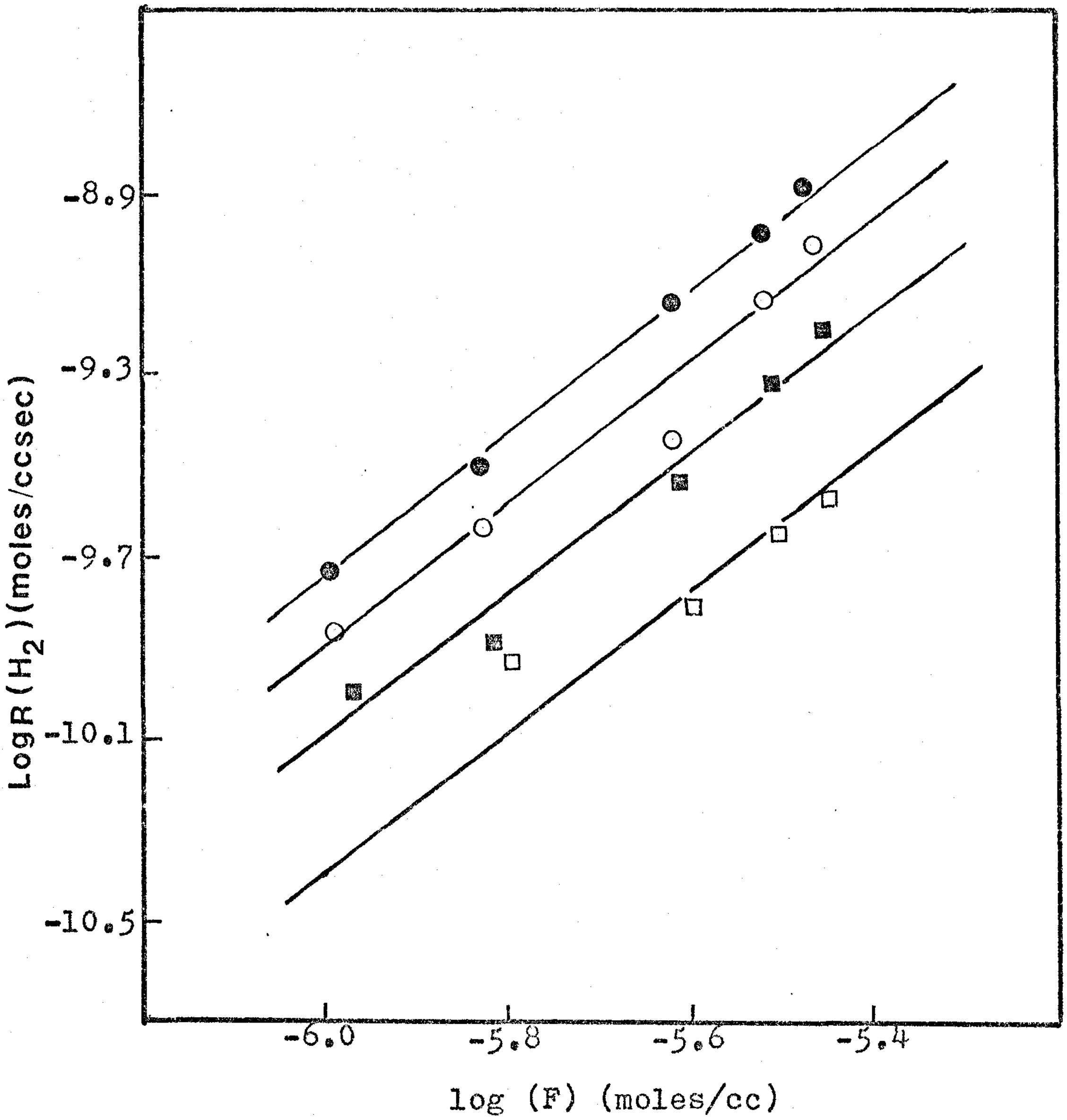

Fig. 6: Log rate of hydrogen production against log formaldehyde concentration at

● 516.6°C

○ 500.0°C

■ 483.2°C

□ 466.3°C

The slopes are all 1.6 .

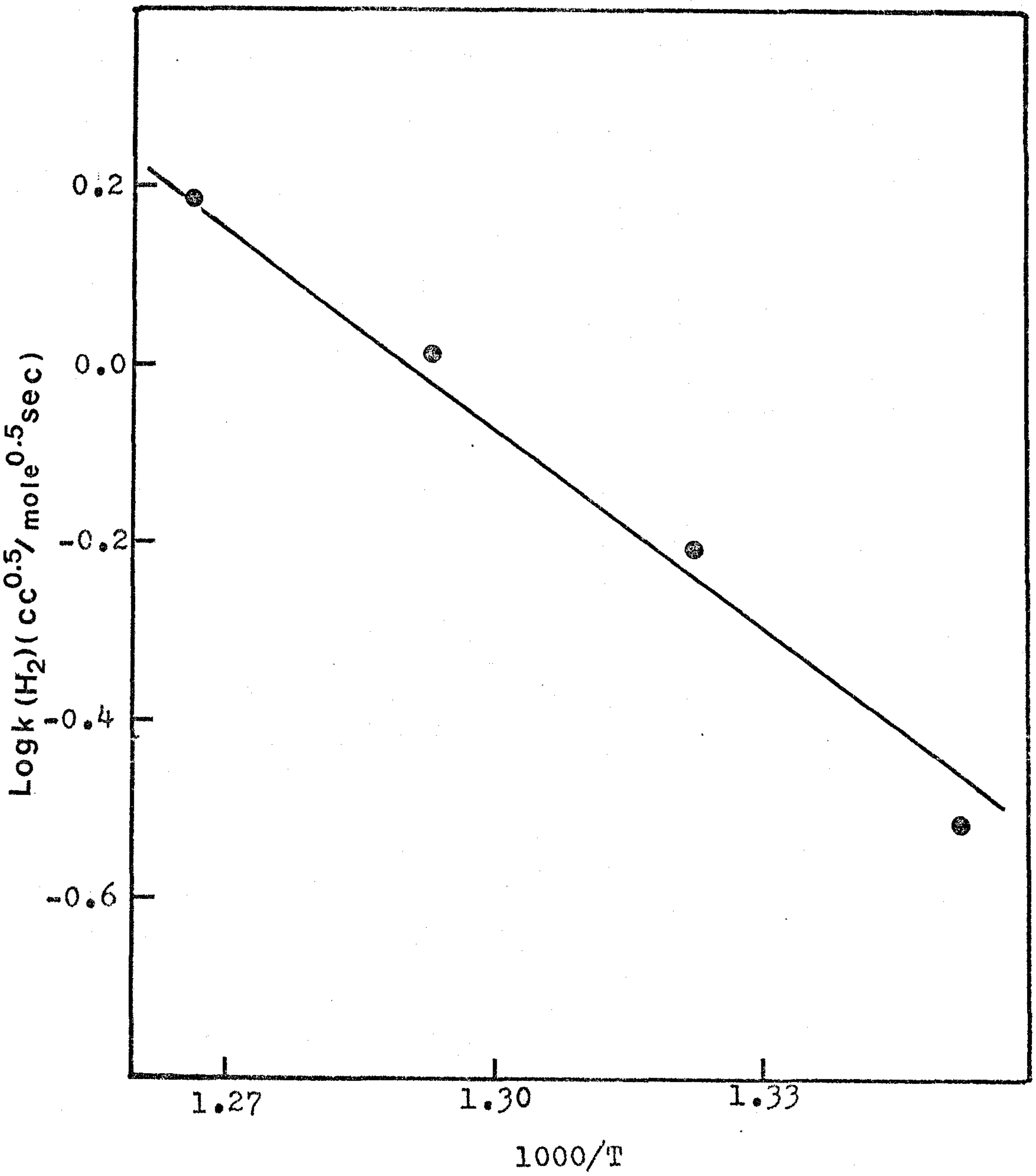

Fig. 7: Arrhenius plot of the rate constants of hydrogen production.

methanol was not carried out in present work due to lack of sensitivity of the analytical system*. Since the rates of methanol formation must be known in order to properly test any postulated mechanism it was decided to estimate these rates in the same manner as was done earlier by Klein et al (6). Since carbon monoxide, hydrogen and methanol are the only products detected so far it was assumed that the rate of methanol formation could be estimated from the difference between the rate of carbon monoxide and hydrogen yields. The plots of log rate of estimated methanol formation against log concentration of formaldehyde are shown in Fig. 8 in which the slopes are approximately equal to 2.0 . The Arrhenius plot (Fig. 12) gives an activation energy and A factor about 36.8 ± 1.0 kcal/mole and 12.6 ± 0.9 cc/mole sec** respectively.

Arrhenius Plots of $R(CO)/F^2$ and $R(H_2)/F^2$.

Typical plots of $R(CO)/F^2$ and $R(H_2)/F^2$ against $1/F^{\frac{1}{2}}$ at 516.6°C are shown in Fig. 9 and Fig. 10 respectively. The results are listed in Table 2 from the plots of carbon monoxide, hydrogen and estimated methanol based on equation [22], [23], and [24] respectively.

Arrhenius plots of $k_3(k_8/k_{16})^{\frac{1}{2}}$ and k_8 for carbon monoxide, hydrogen and estimated methanol are shown in Fig. 11 and

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* A flame ionization detector has now been installed and work is in progress on the analysis of methanol.

** Average deviations from estimated values.

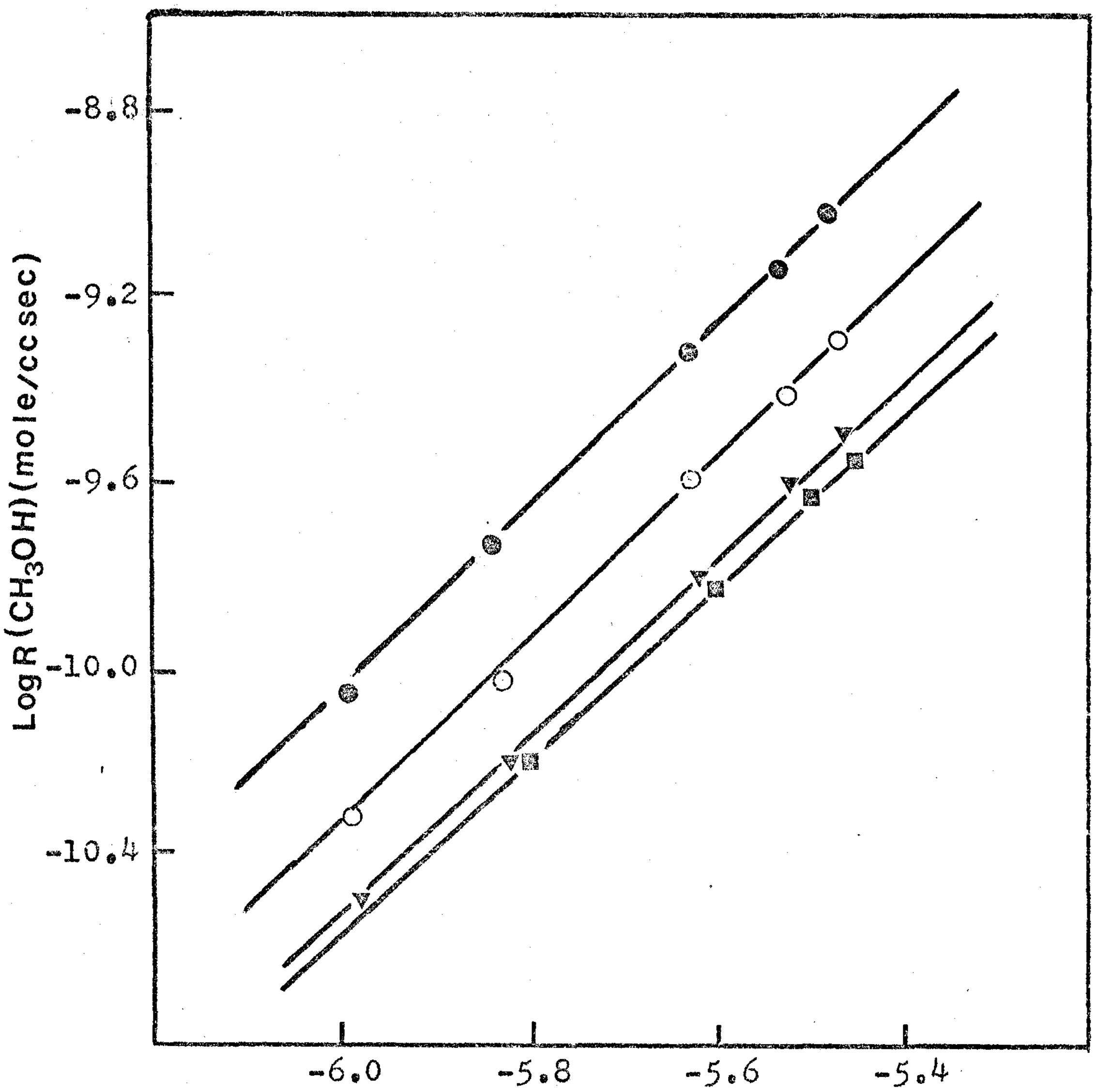

Fig. 8; Log rate of estimated methanol production against log formaldehyde concentration at

● 516.6°C

○ 500.0°C

▼ 483.2°C

▨ 466.3°C

The slopes are approximately equal to 2.0 .

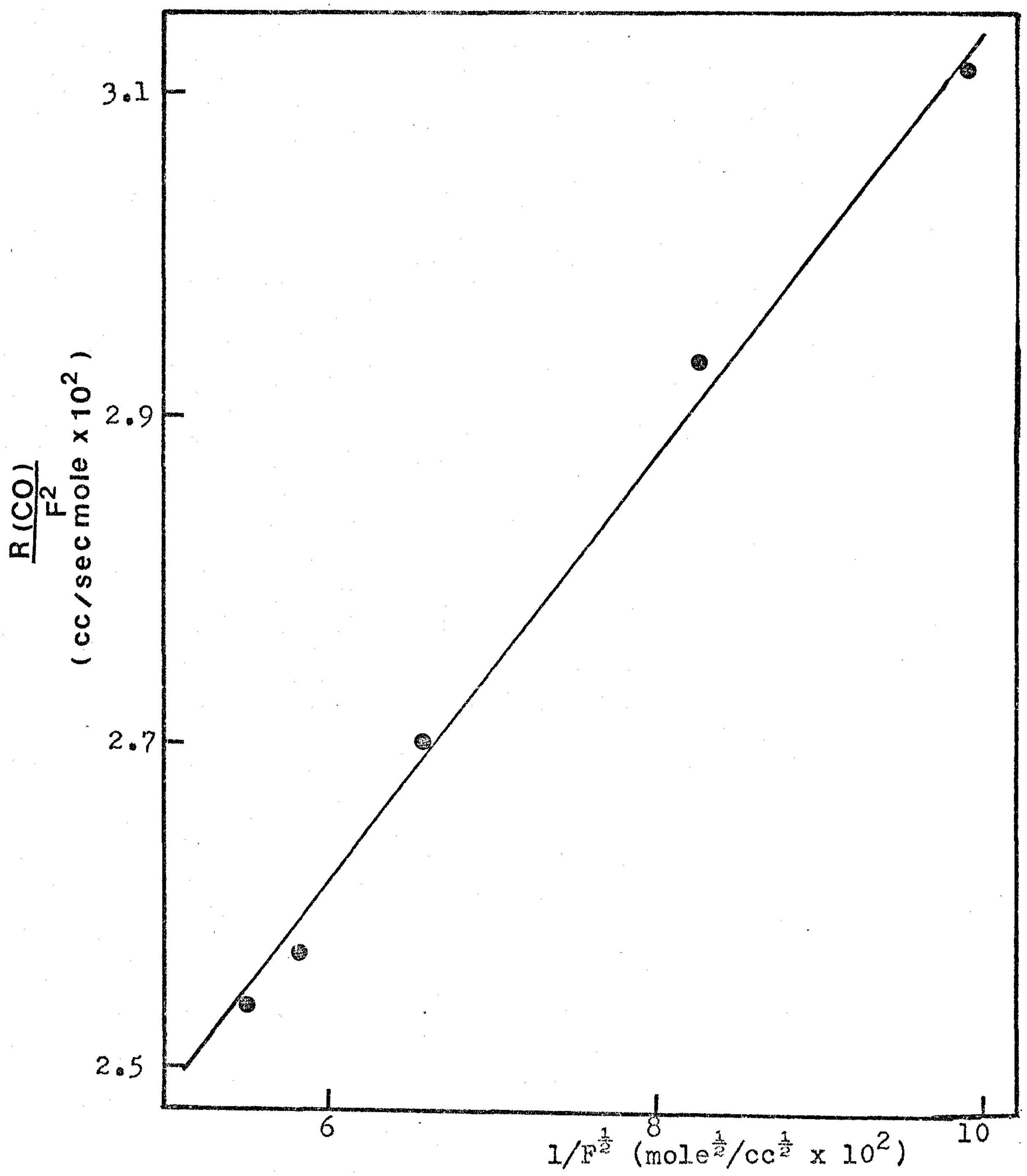

Fig. 9: Typical plot of rate of CO /F^2 against $1/F^{\frac{1}{2}}$ at 516.6°C

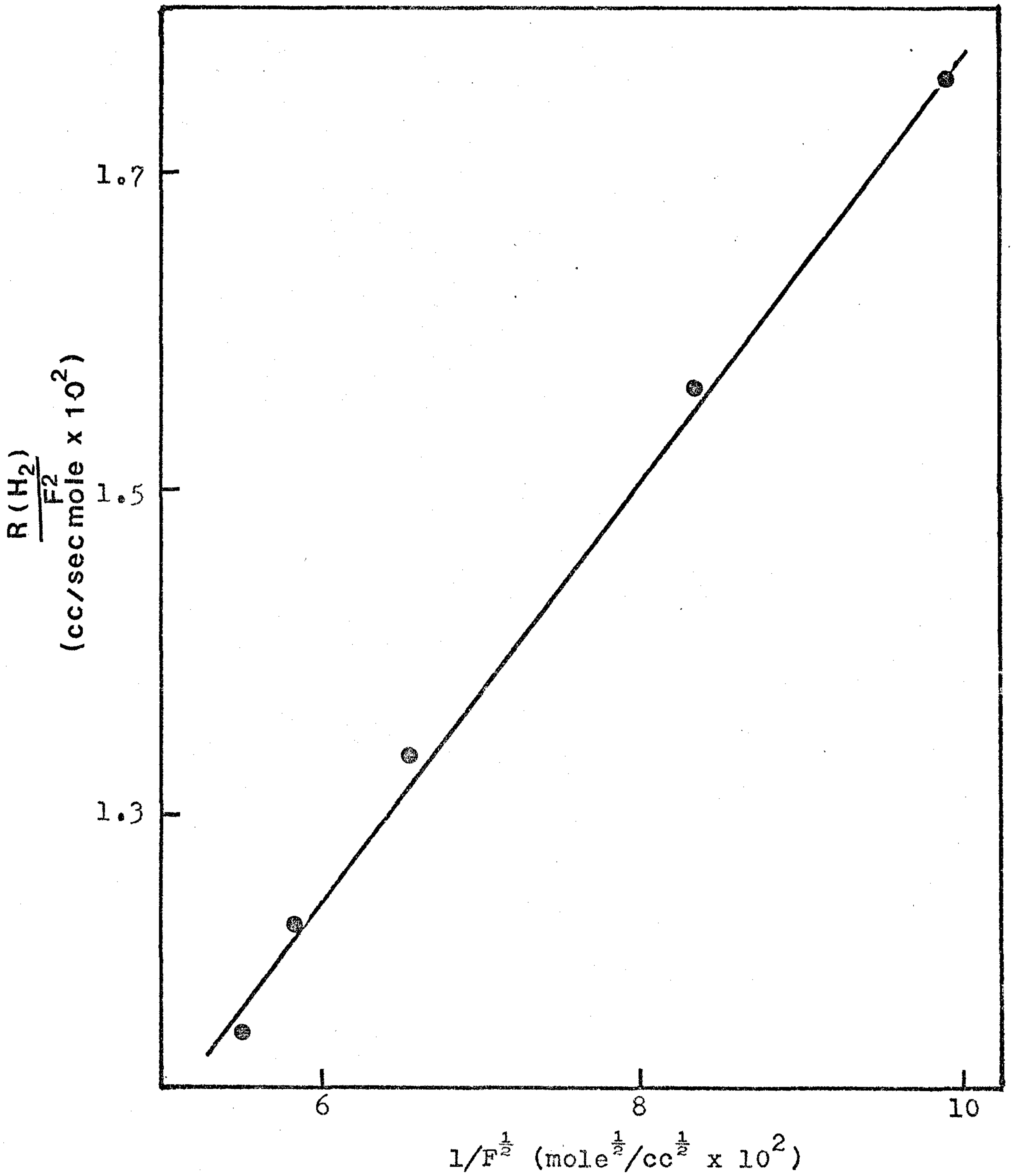

Fig. 10: Typical plot of rate of H_2/F^2 against $1/F^{\frac{1}{2}}$ at 516.6°C

TABLE 2

$k_3(k_8/k_{16})^{\frac{1}{2}}$ and k_8 from the extrapolations of $R(CO)/F^2$, $R(H_2)$ against $1/F^{\frac{1}{2}}$ plots .

T	k'_{CO}	$k_{8_{CO}}$	k'_{H_2}	$k_{8_{H_2}}$	$k^*_{8_{CH_3OH}}$
516.6	0.1345	90.05	0.1303	47.176	115
500.0	0.08868	51.65	0.08338	36.57	58.9
483.2	0.05512	31.19	0.05178	21.29	34.7
466.3	0.03702	20.57	0.02150	12.37	31.0

$k' = k_3(k_8/k_{16})^{\frac{1}{2}}$

* extrapolated from Fig. 8 .

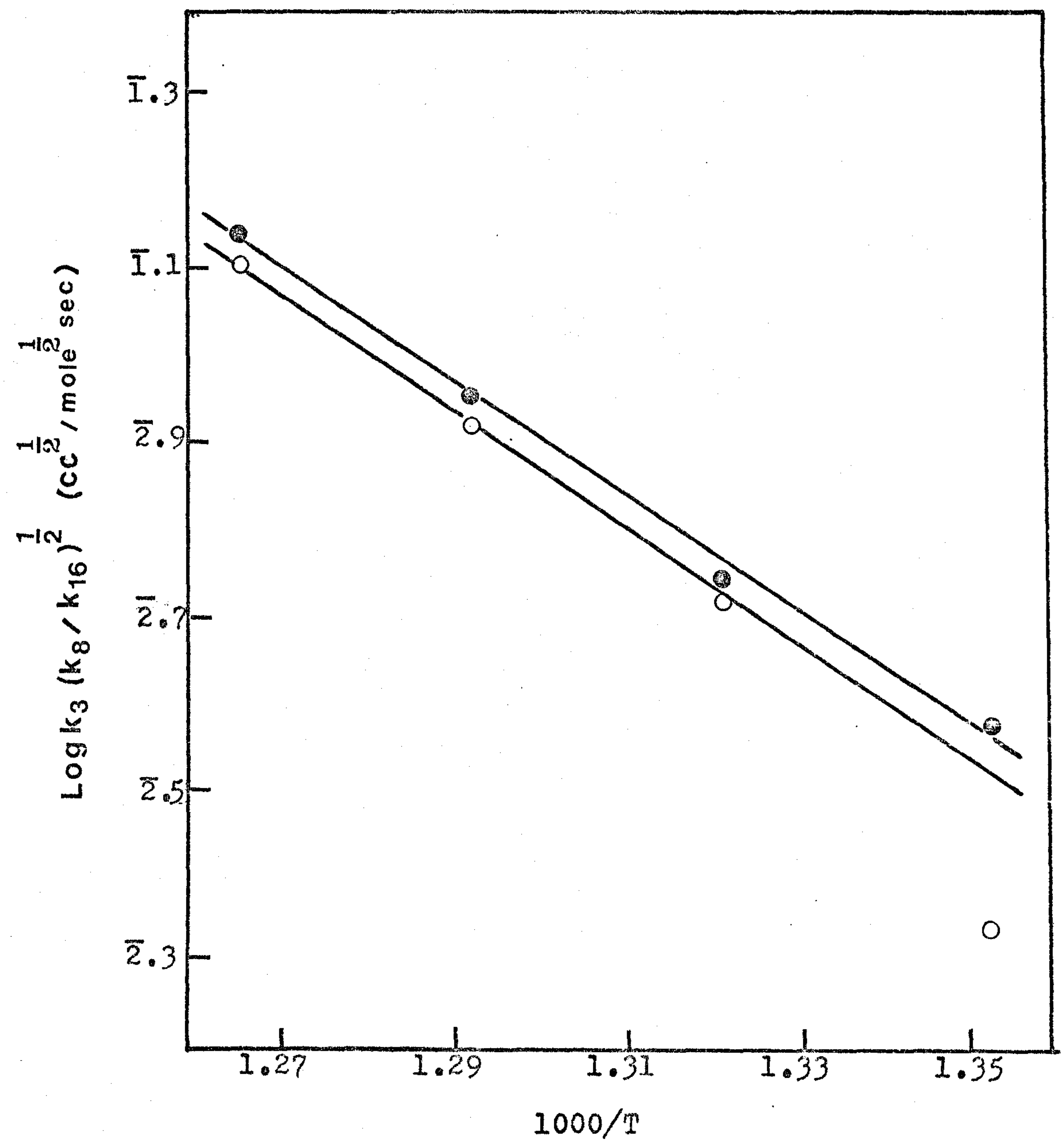

Fig. 11: Arrhenius plot of $k_3(k_8/k_{16})^{\frac{1}{2}}$

● carbon monoxide (from equation [22])

○ hydrogen (from equation [23])

The point at 1000/T = 1.352 is suspect .

Fig. 12 respectively. These plots can be represented by the following equations :

$$\log k_3(k_8/k_{16})^{\frac{1}{2}}_{CO} = (8.4 \pm 0.3) - (32200 \pm 2200)/4.58T \qquad [11]$$

$$\log k_{8_{CO}} = (12.2 \pm 0.6) - (37200 \pm 1200)/4.58T \qquad [12]$$

$$\log k_3(k_8/k_{16})^{\frac{1}{2}}_{H_2} = (8.0 \pm 1.0) - (32600 \pm 1000)/4.58T \qquad [13]$$

$$\log k_{8_{H_2}} = (11.4 \pm 0.3) - (36700 \pm 2750)/4.58T \qquad [14]$$

$$\log k^{*}_{8_{CH_3OH}} = (12.6 \pm 0.9) - (36800 \pm 1000)/4.58T \qquad [14b]$$

* Obtained from estimated $R(CH_3OH)$ against log formaldehyde concentration plot as shown in Fig. 8.

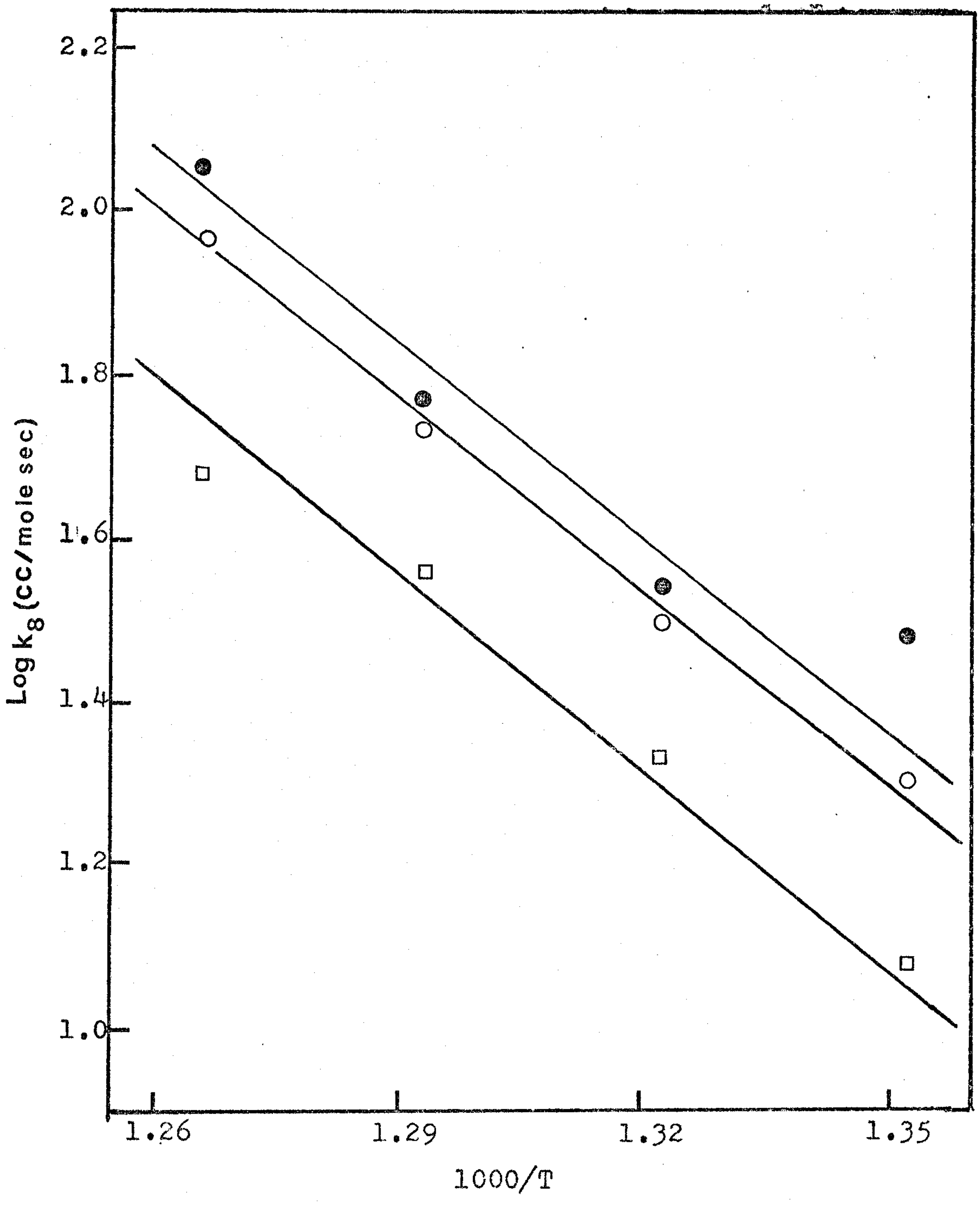

Fig. 12: Arrhenius plot of k_8

○ carbon monoxide (from equation [22])

☐ hydrogen (from equation [23])

● estimated methanol (from equation [24])

DISCUSSION

In view of the results and observations of previous investigators, there is no doubt that the thermal decomposition of formaldehyde occurs predominantly by a chain mechanism. Qualitatively the results of the present work can be explained satisfactorily by the following mechanism. However, the correct mechanism is probably more complicated but more detailed speculation would requir further experimental research. This scheme is a slight modification of Gay et al's (7) mechanism II (page 4).

$$2\,CH_2O \longrightarrow CH_2OH + CHO \qquad [8]$$

$$M + CH_2OH \longrightarrow CH_2O + H + M \qquad [9]$$

$$CH_2OH + CH_2O \longrightarrow CH_3OH + CHO \qquad [15]$$

$$M + CHO \longrightarrow H + CO + M \qquad [3]$$

$$H + CH_2O \longrightarrow H_2 + CHO \qquad [2]$$

$$M + 2\,CHO \longrightarrow 2\,CO + H_2 + M \qquad [16]$$

Application of the steady state approximation leads to the follwing rate expressions:

$$-\frac{d[F]}{dt} = 2k_8[F]^2 + k_{15}\left\{k_8/(k_9[M] + k_{15}[F])\right\}[F]^3 + k_3(k_8/k_{16}[M])^{\frac{1}{2}}[F]^2 \qquad [17]$$

$$\frac{d[CO]}{dt} = k_3(k_8/k_{16}[M])^{\frac{1}{2}}[F][M] + 2\,k_{16}(k_8/k_{16}[M])\,[F]^3 \qquad [18]$$

$$\frac{d[H_2]}{dt} = k_9\left\{k_8/(k_9[M] + k_{15}[F])\right\}[F]^3 + k_3(k_8/k_{16}[M])^{\frac{1}{2}}[F]^2$$
$$+ k_8\ F^{\ 2} \qquad [19]$$

$$\frac{d[CH_3OH]}{dt} = k_{15}\left\{k_8/(k_9[M] + k_{15}[F])\right\}[F]^3 \qquad [20]$$

Where F represents CH_2O and M is a third body.

If $M = F$ and assuming at low temperature that $k_{15} > k_9$, and $k_3 > k_9$, equations [17], [18], [19] and [20] become:

$$-\frac{d[F]}{dt} = 3k_8[F]^2 + k_3\left(\frac{k_8}{K_{16}}\right)^{\frac{1}{2}}[F]^{3/2} \qquad [21]$$

$$\frac{d[CO]}{dt} = 2\ k_8[F]^2 + k_3\left(\frac{k_8}{K_{16}}\right)^{\frac{1}{2}}[F]^{3/2} \qquad [22]$$

$$\frac{d[H_2]}{dt} = k_8[F]^2 + k_3\left(\frac{k_8}{K_{16}}\right)^{\frac{1}{2}}[F]^{3/2} \qquad [23]$$

$$\frac{d[CH_3OH]}{dt} = k_8[F]^2 \qquad [24]$$

Benson (12) recommended $k_3 = 10^{13.7}\exp(-19.0 \text{ kcal/RT})$ and $k_9 = 10^{13.05}\exp(-29 \text{ kcal/RT})$. Constant k_{15} can be estimated as $10^{11}\exp(-6 \text{ kcal/RT})$ by comparison with similar abstraction reactions (13). Therefore at about 500°C, $k_{15}/k_9 \approx 10^4$.

The results of the present work on carbon monoxide yields leads to an order of 1.8 with respect to formaldehyde. This suggests that in equation [22] both terms on the right hand side are important. The reaction order obtained by this work was supported by replotting Fletcher's (3) data which led to 1.7 order dependence on formaldehyde pressure.

The approximate three-halves order dependence observed in the case of hydrogen agrees with equation [23] providing the second term dominates. Equation [22] and [23] are identical except for the factor of 2 appearing in [22]. This accounts for the higher order in the carbon monoxide case. Rate $-\frac{d[F]}{dt}$ could not be determined accurately because of losses in the analysis due to polymerization. Qualitative results however show approximate agreement with equation [21] .

The estimated rate law for methanol production agrees with [24].

Reactions [9], [3], and [16] are assumed to be in their pressure-dependent regions. This assumption can be justified by comparison with three, five and six-atom unimolecular processes (12,14) in approximately the same temperature and pressure range.

Estimation of E_8.

There is a wide variation in the published values of the bond dissociation energy of C-H in formaldehyde. Kinetic studies have led to higher values varying from 87 to 91 kcal/mole (15, 16, 17). On the other hand spectroscopic and electron impact studies produced lower values varying from 75 to 82 kcal/mole (18, 19, 20, 21, 22). The related thermochemical data such as $\Delta H_f^o(CH_2O)$, $\Delta H_f^o(CH_2OH)$ are also uncertain (23, 24). Therefore an accurate estimate of the activation energy of reaction [8] is not possible at the present time. It is worthwhile however to compare these experimental results with that predicted using more recent (23,24) thermochemical data.

The experimental activation energy given by equations [12] , [14] and [14b] should correspond to the activation energy for reaction [8] according to the mechanism. If $\Delta H_f^o\ (CH_2O) = -25.9 \pm 0.11$ kcal/mole (23), $D(H\text{-}CHO) = 88.5 \pm 0.9$ kcal/mole (23), $\Delta H_f^o(CH_2OH) = -8.4 \pm 3.0$ kcal/mole (24) and calculated $\Delta H_f^o(CHO) \approx 10.5$ kcal/mole are chosen the heat of reaction for reaction [8] will be equal to 53.9 kcal/mole. At about 700^oK, $\Delta C_pT_o \approx 1.5$ kcal/mole and assuming the activation energy for backward reaction, $E_{-8} \approx 0$, then $E_8 \approx 52.4$ kcal/mole.

All former investigators obtained lower values (3, 7) compared with this estimated activation energy. The present work leads to a value of about 37 kcal/mole as shown in Fig. 12 and equation [12], [14], and [14b]. It seems unlikely that the experimental value could in error by such an extent. This is supported by extrapolating the results of present work to 547°C for comparison with Klein et al's (6) results. Use of an activation energy of 34.4 kcal/mole and an A factor of 11.78 $cc^{0.8}/mole^{0.8}$ sec as shown in Fig. 4 leads to calculated rates of carbon monoxide formation within less than a factor of two of those observed experimentally. If the low activation energy is correct, the explanation may lie in the uncertain heat of formation or possibly could be a result of a wall reaction in the initiation step. All results of former investigators (4.6), however, showed that the reaction was independent of the surface to volume ratio. Therefore if the initiation step does occur on the wall then there should also be a termination reaction on the wall. This is unlikely however in view of the low overall activation energy obtained in a shock tube by Gay et al (7). Further work particularly on methanol yields should resolve these questions.

APPENDIX I

THE PYROLYSIS OF FORMALDEHYDE
FUNDAMENTAL DATA

Run	P(CH_2O)	Temp	Time	CO	H_2	CO/H_2
	(mm)	(°C)	(sec)	(moles x 10^{-6})		
127	162.0	516.6	45	33.7	15.5	2.1
123	162.0	516.5	30	25.9	11.7	2.2
124	162.0	516.6	20	17.7	8.3	2.1
125	161.0	516.6	10	9.28	4.9	1.8
126	162.0	516.6	6	6.4	3.4	1.8
128	143.0	516.6	30	19.3	10.5	1.8
129	144.0	516.6	20	13.2	4.9	2.6
130	143.5	516.6	11	8.08	3.4	2.3
131	143.5	516.6	6	5.7	3.0	1.9
137	115.0	516.6	45	18.0	9.4	1.9
132	115.0	516.6	30	14.8	7.9	1.8
133	114.8	516.6	30	12.8	6.4	2.0
134	115.0	516.6	20	10.5	5.1	2.0
135	115.0	516.6	10	5.04	3.56	1.4
136	114.5	516.6	7	3.56	2.1	1.6
142	71.5	516.6	45	8.08	4.5	1.7
138	71.5	516.6	30	4.04	3.3	1.2
139	71.0	516.6	20	4.04	2.0	2.0
140	71.0	516.6	10	2.54	1.5	2.6
141	71.5	516.6	6	1.90	1.1	2.7

APPENDIX I

(CONTINUED)

Run	$P(CH_2O)$ (mm)	Temp (^oC)	Time (sec)	CO	H_2	CO/H_2
				(moles x 10^{-6})		
143	50.0	516.6	45	4.00	2.7	1.5
144	50.5	516.6	30	2.76	2.0	1.3
145	49.8	516.6	20	2.36	2.1	1.1
146	50.0	516.6	10	1.18	0.9	1.3
147	50.2	516.6	6	1.60	1.0	1.6
148	50.0	516.6	6	0.84	0.8	1.0
121	161.8	500.0	45	25.4	14.4	1.76
117	162.0	500.0	30	17.5	7.37	2.3
118	162.1	500.0	15	10.1	5.92	1.7
120	161.8	500.0	10	8.24	4.5	1.8
119	162.0	500.0	6	6.04	2.8	2.1
113	143.0	500.0	53	21.9	12.4	1.76
112	143.0	500.0	45	18.4	10.5	1.75
111	143.5	500.0	30	13.4	7.4	1.8
116	143.2	500.0	20	9.44	4.5	2.0
115	143.0	500.0	10	5.8	4.0	1.4
114	143.0	500.0	6	3.48	2.9	1.2
106	115.3	500.0	45	10.2	10.3	1.0
107	115.0	500.0	30	8.40	4.3	1.9
108	115.0	500.0	15	5.04	2.8	1.7
109	115.0	500.0	10	3.28	2.4	1.3
110	115.0	500.0	6	2.72	2.0	1.3

APPENDIX I

(Continued)

Run	$P(CH_2O)$	Temp	Time	CO	H_2	CO/H_2
	(mm)	(°C)	(sec)	(moles x 10^{-6})		
104	71.0	500.0	45	4.88	3.4	1.4
105	71.0	500.0	45	5.00	3.2	1.5
99	70.8	500.0	30	3.95	2.9	1.3
100	70.9	500.0	20	2.44	2.0	1.2
101	71.0	500.0	10	1.25	1.4	0.85
102	71.0	500.0	6	1.12	0.6	1.8
103	71.0	500.0	6	1.12	0.9	1.2
96	50.0	500.0	60	3.90	3.3	1.1
97	50.0	500.0	60	3.46	2.5	1.3
98	50.0	500.0	60	3.84	2.2	1.7
95	50.0	500.0	45	2.90	1.8	1.6
91	50.0	500.0	30	2.02	1.4	1.4
92	50.0	500.0	30	1.94	1.4	1.3
93	50.0	500.0	15	1.20	0.8	1.5
94	50.0	500.0	6	0.62	0.7	0.8
176	161.8	483.2	120	35.04	13.2	2.6
172	161.5	483.2	60	21.76	10.3	2.1
174	162.0	483.2	90	28.48	12.2	2.3
175	162.0	483.2	45	15.36	6.5	2.3
171	161.0	483.2	30	10.96	5.6	1.9
173	162.0	483.2	15	6.68	3.34	2.0

APPENDIX I

(Continued)

Run	$P(CH_2O)$ (mm)	Temp (^oC)	Time (sec)	CO (moles x 10^{-6})	H_2	CO/H_2
181	144.0	483.2	90	25.60	11.8	2.1
180	143.0	483.2	60	17.76	8.02	2.2
177	144.0	483.2	45	13.4	5.3	2.5
179	143.5	483.2	30	9.68	4.5	2.1
178	144.0	483.2	15	5.16	2.8	1.8
168	115.0	483.2	120	17.36	8.4	2.0
169	114.5	483.2	90	14.08	6.9	2.0
170	115.5	483.2	90	14.56	7.1	2.0
166	114.0	483.2	60	8.92	3.6	2.4
167	115.0	483.2	45	7.12	2.73	2.6
164	115.0	483.2	30	4.60	2.1	2.1
165	114.5	483.2	15	2.68	1.58	1.6
162	70.5	483.2	120	7.20	2.88	2.5
163	71.0	483.2	90	5.32	2.07	2.5
161	71.0	483.2	60	3.70	1.94	1.9
159	71.0	483.2	45	2.96	1.61	1.8
157	71.5	483.2	30	3.76	2.42	1.5
158	71.0	483.2	30	1.95	1.41	1.3
160	71.0	483.2	15	1.15	0.86	1.3
154	49.8	483.2	120	4.1	2.5	1.6
155	49.8	483.2	90	3.2	1.6	2.0

APPENDIX I

(Continued)

Run	$P(CH_2O)$	Temp	Time	CO	H_2	CO/H_2
	(mm)	(°C)	(sec)	(moles x 10^{-6})		
156	50.0	483.2	90	3.52	2.1	1.6
150	50.5	483.2	60	2.22	1.8	1.2
149	50.0	483.2	45	2.40	1.9	1.2
151	50.0	483.2	45	1.56	1.4	1.1
152	50.0	483.2	30	1.08	0.72	1.5
153	50.0	483.2	15	0.66	0.34	1.9
191	162.0	466.3	90	19.2	5.03	3.81
193	162.0	466.3	90	18.40	4.08	4.50
189	162.0	466.3	60	12.32	2.32	5.31
188	162.0	466.3	45	10.32	2.33	4.42
182	162.0	466.3	30	6.84	2.09	3.27
183	161.5	466.3	30	7.04	2.10	3.35
184	162.0	466.3	30	7.40	2.89	2.56
185	160.0	466.3	30	7.20	2.95	2.44
186	162.0	466.3	30	7.64	3.19	2.39
187	168.0	466.3	30	7.20	2.52	2.85
190	162.0	466.3	15	3.96	1.89	2.09
192	162.0	466.3	15	4.28	1.67	2.56
198	143.0	466.3	90	16.32	5.00	3.26
197	143.7	466.3	60	11.76	3.08	3.81
196	143.2	466.3	45	8.80	3.07	2.86
194	143.8	466.3	30	6.08	2.45	2.48
195	143.5	466.3	15	3.80	1.48	2.56

APPENDIX I

(Continued)

Run	$P(CH_2O)$	Temp	Time	CO	H_2	CO/H_2
	(mm)	(^oC)	(sec)	(moles x 10^{-6})		
205	115.0	466.3	90	10.80	3.86	2.79
201	115.0	466.3	60	8.48	3.58	2.37
200	115.0	466.3	45	5.52	2.41	2.29
204	115.0	466.3	45	6.32	2.69	2.34
199	115.0	466.3	30	4.76	2.50	1.90
203	115.0	466.3	30	4.44	2.82	1.57
202	115.0	466.3	15	2.60	1.70	1.52
208	71.0	466.3	60	4.52	3.28	1.37
208	71.0	466.3	45	2.50	1.93	1.29
206	70.5	466.3	30	2.44	1.96	1.24
209	71.0	466.3	30	2.12	1.91	1.11
210	71.0	466.3	30	2.22	1.54	1.44
211	71.0	466.3	30	1.88	1.48	1.27

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VITA AUCTORIS

I was born on October 9, 1938 in Taitung, Taiwan, China, where I attended primary and normal high school, and also spent three years teaching in primary school. From 1961 to 1965 I attended Tamkang College of Arts and Sciences in Taipei and recieved my Bachelor of Science in Chemistry. After one year service in Chinese Air Force Artillery, I spent two years teaching chemistry in high school and one year as a teaching assistant in Tamkang College. Since 1969 I have been enrolled in the Graduate School at the University of Windsor.