

# INTERACTION OF CARBON MONOXIDE AND HYDROGEN UNDER SILENT DISCHARGE: PRODUCTION OF FORMALDEHYDE

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THERMOCHEMICAL interaction of carbon monoxide and hydrogen investigated by numerous workers has led to products of some technical importance, *viz.*, a number of saturated and unsaturated hydrocarbons,<sup>1</sup> methyl alcohol,<sup>2</sup> etc. It has been found that the above mixture when subjected to an electric discharge shows a pronounced tendency towards condensation. Thenard and Brodie<sup>3</sup> obtained chiefly methane and some complex oily products. The detection of formaldehyde amongst the above reaction products is due to Losanitsch and Jovitschitsch,<sup>4</sup> and especially Lob<sup>5</sup> and Koenig and Weinig.<sup>6</sup> No quantitative information is available in the literature for the occurrence of the above reaction. Most workers formulated the formation of various complex products from formaldehyde produced as a product of primary reaction. It appeared, therefore, that if the primary products were removed from the sphere of reaction to prevent secondary changes and polymerisations, it might be possible to utilise this process for the preparation of formaldehyde. This has now been achieved by circulating the gases through the reaction vessel and scrubbing off the soluble products.

## APPARATUS

The apparatus used in the preliminary stages of this work<sup>7</sup> consisted of a system of two to six ozonisers connected in parallel and fed by a mixture of carbon monoxide and hydrogen kept in circulation by a 'Cenco' hyvac pump. The effluent gases from the ozonisers were returned to the gas reservoir after washing them off the soluble products. The experiments were conducted at constant volume and as the gas mixture suffered condensation during the progress of the reaction, a considerable fall in the pressure resulted. This fall has been found to reduce appreciably the rate of the reaction. Only detectable quantities of formaldehyde resulted. No

improvement in yield could be brought about by the application of catalysts or by altering the rate of circulation. The apparatus was therefore modified to work at constant pressure.<sup>8</sup>

The circuit and the arrangement adopted finally are shown in Fig. 1. It consisted chiefly of a reservoir system and an arrangement for the circulation of the gas mixture. The former served for storing the gases and also

FORMALDEHYDE FORMATION, FROM CO, H<sub>2</sub> UNDER SILENT DISCHARGE

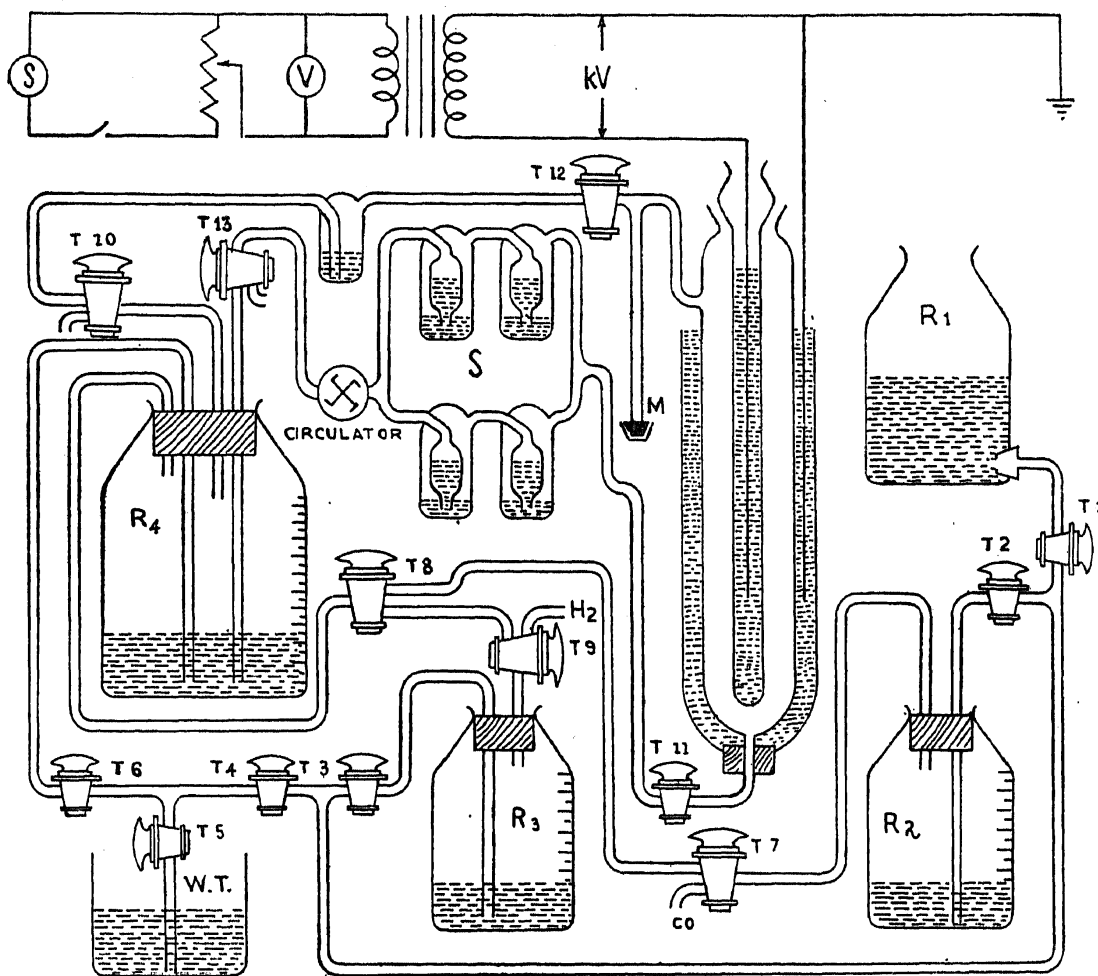


FIG. 1

for preparing a mixture of the two in the desired proportion and consisted of four reservoirs R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> and a water trough W. T. connected with one another by means of glass-stoppers. R<sub>1</sub> was placed on a higher level than the other reservoirs; as a result water flowed from it to any other part of the reservoir system. R<sub>2</sub> and R<sub>3</sub>, each graduated and of 13 litres capacity and R<sub>4</sub> also graduated and of 2.6 litres capacity served for storing carbon monoxide, hydrogen and the gas mixture respectively. By admitting water from R<sub>1</sub>, gas from any of the reservoirs R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> could be displaced.

The circulation system was a closed one in which the gas mixture was kept in constant circulation at a uniform rate at atmospheric pressure. It included the mixture reservoir  $R_4$ , a Siemens' glass ozoniser, a mercury manometer  $M$ , a system of water wash traps ( $S$ ) and a circulator, connected serially. A 'Cenco' hyvac pump with its suction end connected to the water traps and the exhaust end to the reservoir served to circulate the gases. It could also be used for evacuating parts of the circulatory system. By changing the potential applied to the pump, its speed could be altered at will. The rate of circulation at different potentials was determined separately.

Alternating current of 500 cycles frequency obtained by means of a 2 kVA motor alternator set worked off 220 volt D.C. mains, was fed to the primary of a transformer of step-up ratio 150. The primary potential was regulated by means of a variable resistance in its primary. One of the secondaries was earthed; the other was dipped in the salt solution forming the inner electrode of the ozoniser. The other electrode was earthed.

Carbon monoxide was prepared by the action of hot conc. sulphuric acid on oxalic acid and purified by repeatedly passing through a strong solution of potassium hydroxide.  $R_2$  which had been filled with water from  $R_1$  through the taps  $T_1$  and  $T_2$  was connected to the stock of carbon monoxide through the tap  $T_7$ . The water displaced by carbon monoxide from  $R_2$  passed through the taps  $T_4$  and  $T_5$  to the water trough W.T. Hydrogen obtained from a commercial cylinder was purified by bubbling through alkaline pyrogallol solution and was admitted to  $R_3$  by operating the stop-cock  $T_9$ .  $R_4$  was initially filled with water through the taps  $T_1$ ,  $T_4$  and  $T_6$ . By admitting water from  $R_1$  through the taps  $T_1$  and  $T_2$  to  $R_2$ , a desired quantity of carbon monoxide was displaced to  $R_4$ , through the taps  $T_7$  and  $T_8$ . Similarly, hydrogen was displaced through the taps  $T_8$  and  $T_9$ . The water displaced from  $R_4$  in filling up these gases was carried to the trough through the taps  $T_6$  and  $T_5$ . Thus a mixture of carbon monoxide and hydrogen in the desired proportion could be obtained in  $R_4$ . The tap  $T_{10}$  was closed and the ozoniser and the scrubbers were evacuated with the help of the circulator through the three-way tap  $T_{13}$ . An experiment was commenced only after the entire assembly was tested for vacuum; and after rinsing it repeatedly with the reaction mixture.  $R_4$  was then included in the circuit by opening the taps  $T_{10}$  and  $T_{13}$ . With the gases circulated and exposed to the discharge in the ozoniser excited at the desired potential,  $R_4$  was connected to the water trough W.T., through the taps  $T_6$  and  $T_5$ . This served to maintain a constant pressure regime in the part of the system subjected to the circulation of the reaction mixture. Volume changes were noted by observing the level of water inside the reservoir from time to time.

At the end of an experiment, the water from the traps was collected, measured and estimated for formaldehyde, by Romijn's potassium cyanide method.<sup>9</sup> The results of a typical analysis are as follows (*vide* Table I, Expt. No. 3). 100 c.c. of the solution was mixed with 20 c.c. of say N/20 KCN. This was then added to 25 c.c. of N/20 AgNO<sub>3</sub>, acidulated with HNO<sub>3</sub>. The excess of this last was titrated against N/20 NH<sub>4</sub>CNS. The required volume was 19.5 c.c.

By a previous titration, it was found that a mixture of 25 c.c. of AgNO<sub>3</sub> and 20 c.c. of KCN required 2.4 c.c. of NH<sub>4</sub>CNS. The 100 c.c. of formaldehyde solution was therefore equal to (19.5-2.4) 17.1 c.c. of NH<sub>4</sub>CNS. Formaldehyde present is, therefore, 0.046 gm.

RESULTS AND DISCUSSION

*Influence of Composition of the Gas Mixture.*—Pure carbon monoxide also suffered condensation under silent electric discharge.<sup>10</sup> It appeared, therefore, that if the gas mixture contained a greater proportion of hydrogen, it might favour the reaction of carbon monoxide and hydrogen.

At a constant rate of circulation of 8 litres of reaction mixture per minute, with an applied potential of 9.6 kV and 500 cycles, experiments were conducted with gas mixtures in the ratio of 1:0.5 to 1:3 of carbon monoxide and hydrogen respectively. All the experiments were conducted for a period of six hours exposure to discharge. The results are shown in Table I and (in part with reference to the net amount of formaldehyde

TABLE I. *Influence of the Composition of the Gas Mixture*

Expt. No.	Ratio CO:H <sub>2</sub> (% of CO in the mixture)	Volume in c.c. of gases circulated (wt. in gm.)	Volume reduction in c.c.	Yield of formaldehyde		
				c.c. of NH <sub>4</sub> CNS N/20	in gm.	Percentage
1	2	3	4	5	6	7
1	1 : 0.5 (66)	2800 (2.238)	780	22.0	0.033	1.51
2	1 : 0.9 (52.5)	3140 (2.035)	785	31.0	0.046	2.23
3	1 : 1 (50)	2730 (1.711)	670	30.5	0.046	2.7
4	1 : 1.5 (40)	3100 (1.574)	575	24.7	0.037	2.4
5	1 : 2 (33)	2860 (1.261)	660	23.9	0.036	2.84
6	1 : 3 (25)	2900 (1.024)	785	21.1	0.032	3.1

formation and that expressed as a percentage of the mass of the original mixture) graphically in Fig. 2.

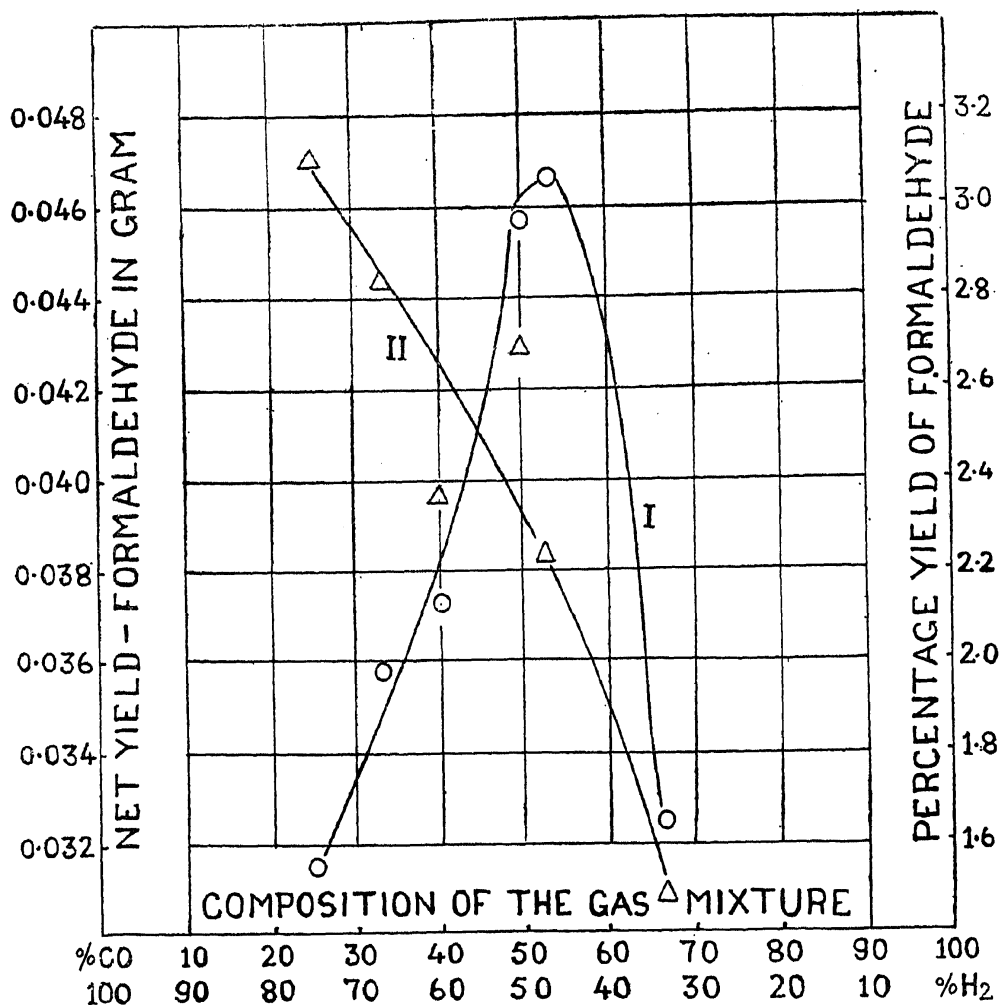


FIG. 2

The absolute yield, *viz.*, 0.046 gm. obtained was highest with an approximately equimolecular mixture of the constituent gases (Fig. 2, Curve 1). The results of experiments 4, 5 and 6 show that the yield of formaldehyde falls with an increased proportion of hydrogen in the mixture although the total reaction between the gases has been greater as shown by the reduction in gas volume (column 4). This may be attributed to an extended hydrogenation of formaldehyde—the product of primary reaction.

In contrast with the above results, the percentage yield (column 7), *i.e.*, the amount of formaldehyde expressed as percentage of the total weight of the gases circulated (column 3) shows a linear dependence with the proportion of hydrogen in the mixture (Fig. 2, Curve 2). The anomaly is only apparent, because an increased proportion of hydrogen results in a corresponding decrease in the proportion of carbon monoxide—the heavier constituent—thereby lowering the weight of the starting materials. Thus, a smaller weight of formaldehyde when represented as percentage of a relatively very much smaller weight of gas mixture appears greater. For instance,

the yields of formaldehyde in experiments 5 and 6 are 0.036 and 0.032 gm. respectively. Expressed as percentages of the initial weight of gases used, viz., 1.261 and 1.029 gms. respectively, these figures appear as 2.84 and 3.1%.

At lower concentrations (column 2) of carbon monoxide, a larger proportion of it is converted into formaldehyde. This is indicated by the increased percentage yield figures. In experiments 3 to 6, where the concentration of carbon monoxide in the mixture is reduced from 50% to 25%, the percentage yield increases from 2.7 to 3.1%. The increase is, however, of little practical significance because for a comparatively small increase, a relatively large proportion of the gas mixture is lost in the form of secondary products.

The results of experiments 1 and 2, in which a larger proportion of carbon monoxide is used, in general, support the above conclusions.

It appears, from the above results, that the presence of very large excesses of one or the other of the constituents affects the yields adversely. At higher concentrations of hydrogen, secondary hydrogenation of carbon monoxide or/and formaldehyde probably takes place; with an excess of carbon monoxide, self condensation occurs lowering considerably the possibility of the reaction  $\text{CO} + \text{H}_2 \rightarrow \text{HCHO}$ .

*Influence of the Rate of Circulation.*—Behaviour of carbon monoxide-hydrogen mixtures in sealed ozonisers indicated that the rate of the reaction is maximum in the early stages of the discharge. It appeared that there was an optimum duration of exposure. As this latter could be varied by changing the rate of gas flow, an attempt was made to determine the appropriate circulation rate.

Experiments were conducted with gas mixtures in 1:1 ratio, at an applied potential of 9.6 kV and 500 cycles frequency with circulation rates of 8, 12, 14 and 24 litres per minute. The results are shown in Table II.

TABLE II. *Influence of the Rate of Circulation*

Exp. No.	Rate of circulation litres per min.	Wash traps in series	Mercury level in the manometer in mm. (pressure in the ozoniser)	Volume of the gases c.c. (Wt. in gm.)	Reduction volume c.c.	Yield of formaldehyde	
						In gm.	Percentage
1	8	2	25 (735)	2730 (1.711)	670	0.046	2.7
2	12	2	35 (725)	2800 (1.714)	630	0.036	2.1
3	14	3	60-70 (690-700)	3000 (1.836)	775	0.041	2.2
4	24	3	160-170 (590-600)	2980 (1.822)	470	0.031	1.7

As indicated by the reduction in volume and the yield of formaldehyde in experiments 1 and 2, and 3 and 4, an increased rate of circulation, above 8 litres per minute does not favour the production of formaldehyde.

Preliminary results<sup>8</sup> suggested that the efficiency of the removal of formaldehyde from the gases falls off at higher rates of circulation. Experiments 3 and 4 were therefore conducted with three wash traps instead of two, used previously. The yield of formaldehyde in experiment 3 is higher than that of experiment 2, although in the former case, the rate of circulation is greater.

It will be seen (Table II, column 4) that at higher rates of circulation, the operative pressure inside the ozoniser falls progressively, owing to the increased suction. For instance, in experiment 1, it is 735 mm. whereas in experiment 4, it is about 600 mm. It is probable that this diminution in the operative pressure may be a factor contributing to lower yields at higher rates of circulation (*cf.*, Influence of Potential).

*Influence of the Size of the Ozoniser.*—An increased rate of circulation diminishes the duration of exposure to discharge but interferes with the absorption of formaldehyde (*vide supra*). It appeared, that at a constant rate of circulation, a variation in the length of the ozoniser would change the former without affecting the latter.

Experiments were conducted with 6", 9" and 12" long ozonisers with a circulation rate of 8 litres/minute, 9.6 kV and 500 cycles frequency. The results are shown in Table III.

TABLE III. *Influence of the Size of the Ozoniser*

Expt. No.	Length of the ozoniser inches	Volume of the gases c.c. (wt. in gm.)	Reduction in volume c.c.	Yield of formaldehyde	
				in gram	Percentage
1	2	3	4	5	6
1	6	3000 (1.809)	425	0.031	1.72
2	9	3000 (1.848)	640	0.035	1.91
3	12	3000	695		

A decrease in the ozoniser length is tantamount to an increase in the rate of circulation. It is to be expected from the results of Table II that the yield of formaldehyde should fall with the length. The experimental results are in accord with this deduction. It is interesting to observe, however, that although the reduction in volume in experiment 2 is greater by

about 50% than in experiment 1, the increase in the yield of formaldehyde is only 14%. This is in agreement with the earlier conclusion (*vide* Influence of rate of circulation) that a greater duration of exposure to discharge results in the destruction of formaldehyde initially formed.

It is felt that further work is necessary to define optimum conditions with respect to the size of the ozoniser.

*Influence of Excitation Potential.*—According to Joshi,<sup>11</sup> the quantity  $V-V_m$  only is significant for a discharge reaction,  $V$  and  $V_m$  being the applied and threshold potentials respectively. As a general observation, it has been known that an increase in  $V-V_m$  results in an increased rate of reaction. Experiments were carried out at 6.0, 6.75, 7.5, 9.6 and 10.5 kV of 500 cycles frequency at a gas flow of 8 litres per minute. The results are shown in Table IV.

TABLE IV. *Influence of Excitation Potential*

Expt. No.	Applied potential kV	Duration of the discharge in min.	Volume of the gases c.c. (wt. in gm.)	Reduction in volume c.c.	Yield of formaldehyde	
					in gm.	Percentage
1	2	3	4	5	6	7
1	6.0	120	2800	..	..	..
2	6.75	120	2800	..	..	..
3	7.5	120	2870	210	..	..
4	9.6	360	2730 (1.711)	670	0.046	2.7
5	10.5	360	2770 (1.698)	725	0.037	2.17

It will be seen that below the threshold potential of 7.5 kV, there is no reaction. In experiments 4 and 5, the reductions in volume are 665 and 725 c.c. respectively. Thus the overall reaction velocity is greater at 10.5 kV than 9.6 kV as is to be expected. The yield of formaldehyde, on the other hand, is found to be greater by about 25% at the lower exciting potential. It is suggested, therefore, that the formaldehyde initially formed undergoes secondary changes to a greater extent at higher applied potentials.

It is probable that in experiments, where the rate of circulation is varied, a fall in the operative gas pressure (*vide supra*, Table II, column 4) resulted in a lowering of the  $V_m$  and consequently in an increase of  $V-V_m$ . This would have an unfavourable effect on the yield of formaldehyde and may, in fact, be a factor contributing to the observed decrease at higher rates of circulation.



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#### SUMMARY

Production of formaldehyde by the interaction of carbon monoxide and hydrogen under silent discharge at 500 cycles frequency has been investigated with respect to (1) the gas composition, (2) the rate of circulation, (3) the ozoniser size and (4) the excitation potential. The gas mixture was circulated through the reaction vessel at atmospheric pressure and formaldehyde was removed from the effluent gases by scrubbing through water wash traps. The optimum values for formaldehyde formation in respect of factors 1 to 4 have been determined. An increase above this value of 2 decreases the yield due to (in part) incomplete absorption of the product. A larger ozoniser size increases the net yield but entails a waste of the reacting mixture. Increase of the excitation potential increases the velocity of the change but reduces the yield due to secondary changes in the formaldehyde produced. Equimolecular mixtures of the reacting gases with optimum values under 2, 3 and 4 correspond to 0.046 gm., i.e., 16 gm. per KW-hour.

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