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

PART II. INFLUENCE OF TEMPERATURE

BY R. H. SAHASRABUDHEY, M.SC., PH.D.
(*Assistant Professor in Chemistry, Chemistry Department, Benares Hindu University*)
AND
S. M. DESHPANDE, M.SC.
(*J. K. Fellow, Benares Hindu University*)

Received October 11, 1949
[Communicated by Prof. S. S. Joshi, D.SC. (Lond.), F.A.SC.]

INFLUENCE of a number of factors, *viz.*, gas composition, ozoniser size, circulation rate, etc., on the interaction of CO and H_2 under silent electric discharge leading to the formation of formaldehyde has been already investigated.[8] The reaction $CO + H_2 \rightarrow HCHO$ is slightly exothermic,[11] and as one of the principal methods (*viz.*, that from methyl alcohol) of the manufacture of formaldehyde is a thermal process,[11] it appeared of interest to study the influence of temperature on the present reaction under electrical discharge.

EXPERIMENTAL

The general arrangement of the apparatus and the electrical circuit were the same as in previous experiments.[8] The discharge tube as usual consisted of an ordinary all glass Siemens' ozoniser. To effect the temperature control it was surrounded with a glass jacket provided with a loop similar to the Thiele's melting point bath. This jacket was filled with water, the temperature of which could be maintained at a particular level by carefully heating the side-loop. The temperature of the bath was measured with the help of an ordinary thermometer kept immersed in the bath.

To maintain the comparability of the results, the experiments were carried out under the conditions already described,[8] *viz.*, about 3,000 c.c. of gas mixture (CO : H_2 as 1 : 1) were circulated at the rate of 5 and 8 litres per minute through the ozoniser excited by an A.C. supply of 7·2 kV and 9·6 kV respectively, and 500 cycles frequency. The effluent gases before being returned to the gas holder were passed through three absorbers connected in series to wash them off the soluble products. Duration of an experiment was six hours exposure to discharge. At the close of an experiment the liquors from wash traps were estimated for formaldehyde and acidity and the residual gas analysed with an Orsat's apparatus with the usual absorbants for CO, CO_2 and unsaturated hydrocarbons.

Experiments were conducted at 25, 45, 60 and 80° C. The results are shown in Tables I to IV and graphically in Fig. 1.

TABLE I

Influence of Temperature

Applied Potential .. .. 7·2 kV.
Rate of circulation of gases .. .. .. 5 litres per minute.

Exp. No.	Temp. °C.	Gas mixture circulated c.c. (wt. in gm.)	Gas used up % (c.c.)	Yield of Formaldedyde			Acidity N/25 NaOH c.c.
				c.c. of NH_4CNS N/19·6	gm.	Percentage	
1	2	3	4	5	6	7	8
1	22–25 C°	2655 (1·6339)	20·27 (538)	63·95	0·09787	5·988	18·9
2	45–50°	2950 (1·8151)	25·86 (763)	65·95	0·1009	5·558	24·0
3	60·65°	2900 (1·7851)	26·10 (757)	65·73	0·1006	5·636	22·1
4	80–85°	2918 (1·7968)	32·15 (938)	84·6	0·1322	7·355	31·8

TABLE II

Influence of Temperature

Applied Potential .. .. 9·6 kV.
Rate of circulation of gases .. .. .. 8 litres per minute.

Exp. No.	Temp. °C.	Gas mixture circulated c.c. (wt. in gm.)	Gas used up % (c.c.)	Yield of Formaldehyde			Acidity N/25 NaOH c.c.
				c.c. of NH_4CNS N/19·6	gm.	Percentage	
1	2	3	4	5	6	7	8
1	25°	2870 (1·7668)	27·87 (800)	27·4	0·04193	2·373	7·86
2	45–50°	2616 (1·6104)	29·74 (778)	27·34	0·04185	2·065	17·01
3	60°	2626 (1·6167)	30·66 (805)	28·02	0·04289	2·653	27·73
4	80°	2929 (1·8031)	32·13 (941)	36·39	0·05569	3·089	29·92

TABLE III

Analysis of the Residual Gas Mixture

Exp. No.	Temp. °C.	% of CO_2	% of Unsat. compounds	Percentage of CO	Percentage of H_2+ hydrocarbons
1	2	3	4	5	6
1	22–25°	1·5	1·2	49	48·3
2	45–50°	1·58	1·35	48·42	51·35
3	60–65°	1·68	4·1	43·53	50·31
4	80–85°	3·47	4·93	43·44	48·16

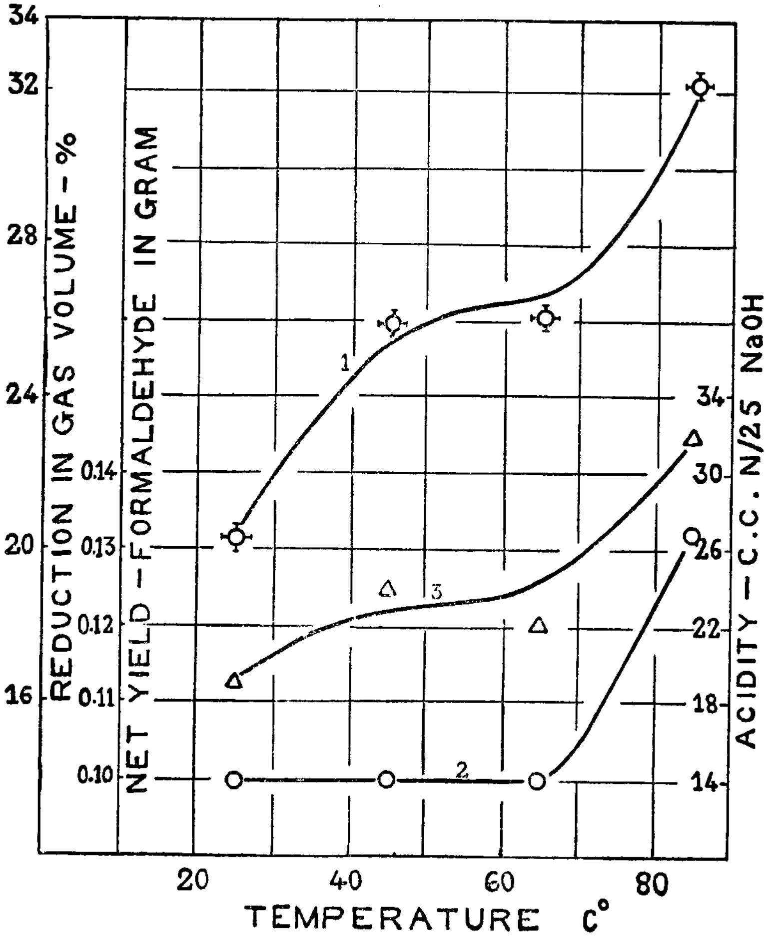

FIG. 1

TABLE IV

Summary of Results

Exp. No.	Residual gas c.c.	Analysis of the residual gas					HCHO gm.	Acidity calculated as HCOOH gm.	Total wt. accounted gm. (Columns 3-9)	Wt. of the starting gas mixture gm.	Wt. Unaccounted for gm.
		CO_2 gm.	Unsat. hydrocarbon (C_2H_4) gm.	CO gm.	CH_4* gm.	H_2 gm.					
1	2	3	4	5	6	7	8	9	10	11	12
1	2117	0·05735	0·02919	1·1920	0·02345	0·08130	0·09787	0·03478	1·51594	1·6339	0·11796
2	2187	0·06241	0·03393	1·217	0·02554	0·08935	0·1009	0·04417	1·5733	1·8151	0·2418
3	2143	0·06501	0·1009	1·072	0·0266	0·08553	0·1006	0·04067	1·49131	1·7851	0·29379
4	1980	0·1241	0·1121	0·9886	0·05076	0·07263	0·1322	0·05852	1·53891	1·7968	0·25789

* Calculated on the basis of CO_2[9].

DISCUSSION OF THE RESULTS

It will be apparent from the figures in column 4 of Tables I and II that the velocity of the reaction, as judged from the percentage reduction in gas volume, goes on increasing steadily with temperature (Fig. 1, Curve 1). In the two sets of experiments the reduction was 20·27% and 27·87% at 25° C. and 32·15% and 32·13% at 80° C. respectively. This increased reaction is, however, not reflected in an increased yield of formaldehyde which is markedly constant but for at the high temperature (80° C.) where it shows some considerable increase (Fig. 1, Curve 2).

A rise in temperature of a gaseous reaction system, as a general rule, results in an increased reaction velocity. This may be due either to (i) an augmented excitation of the reacting entities (atoms and molecules),[4] (ii) due to an increased number of collisions amongst the reacting particles because of the increased kinetic energy, and (iii) in the case of endothermic reactions on account of the increased supply of heat energy.

The temperature range covered in the present instance is comparatively restricted, *viz.*, 25° C. to 80° C., therefore, any considerable thermal excitation leading to an increased reaction velocity does not appear likely. It is more probable that the increased reaction might be due to the increased kinetic energy and the consequent increase in the encounters of CO and H_2 molecules. The reaction, $CO + H_2 \rightarrow HCHO$ is slightly exothermic and therefore, it is to be expected that an increase in temperature would have an unfavourable effect on the above reaction. It has been already pointed out that in spite of an increase in the total reaction (*vide* Tables I and II, column 4) with temperature, the amount of formaldehyde obtained is very nearly a constant quantity (column 6). Pure formaldehyde vapours diluted with an indifferent gas like nitrogen when subjected to moderate temperature is known not to undergo polymerisation.[10] Further, in the thermal process of the manufacture of formaldehyde by the oxidation of methyl alcohol the reaction takes place practically at red heat. It is evident, therefore, that a higher temperature does not have a destructive effect on the formaldehyde formed, but on the contrary might have a depolymerising influence[1] as is perhaps, indicated by slightly better yields at 80° C.

In Table III are shown the results of the analysis of the residual gas at different temperatures. It will be seen that but for a small quantity of CO_2 and unsaturated hydrocarbons the proportion of $CO : H_2$ corresponds very nearly to that of the original gas mixture (*vide infra*). This, indeed, is remarkable in view of the six hours discharge to which a relatively small quantity (3 litres) of gas has been subjected, and is, perhaps, indicative of the reaction $CO + H_2 \rightarrow HCHO$ as the primary reaction.

The residual quantity of CO is slightly lesser than that of the hydrogen (column 5, Table III), but this difference is reasonably accounted for by the quantities of CO_2 and unsaturated hydrocarbons. This is suggestive of the fact that in presence of hydrogen, self-condensation of CO is not considerable.

CO_2 has been assumed by Wendt and Evans[9] to be formed according to the reaction $2CO + 2H_2 \rightarrow CO_2 + CH_4$ and by Crespi and Lunt[2] according to the reaction $4CO \rightarrow C_3O_2 + CO_2$. But, since very small quantities of CO_2 have been detected in the residual gas it might be safe to assume that both these reactions are not taking place to any considerable extent. The probability of CO_2 combining with H_2 to form acids and other condensates is no doubt there, but in view of the almost constant quantity of hydrogen in the residual gas at all the temperatures studied and the increasing quantities of CO_2, this last does not appear of any great significance.

The formation of unsaturated hydrocarbons does not appear to have been observed by earlier workers. The quantities formed are greater than those of CO_2 and show an increase with temperature. These, in the system under examination, might arise in three possible ways:

I. $CO + H_2 \rightarrow HCHO$
$HCHO + HCHO \rightarrow CH_2OH\cdot CHO$[3, 5] (Aldol condensation)
$CH_2OH\cdot CHO + H_2O \rightarrow CH_3OH + HCOOH$
$CH_3OH \rightarrow CO + CO_2 + C_2H_4 + CH_4 + C_2H_2 + H_2$[7]

II. $4CO \rightarrow C_3O_2 + CO_2$[2]
$C_3O_2 + 2H_2O \rightarrow CH_2(COOH)_2 \rightarrow CH_3COOH$
$CH_3COOH \rightarrow CO + CO_2 + C_2H_4 + CH_4 + H_2$[7]

III. $CO + 2H_2 \rightarrow CH_3OH$
$CH_3OH \rightarrow CO + CO_2 + C_2H_4 + CH_4 + C_2H_2 + H_2$[7]

Since the possibilities (i) of the formation of carbon suboxide (*vide supra*) and (ii) of the occurrence of third order reactions in a gaseous phase are limited, the first mechanism appears to us as the most probable. This view finds support in the observation of Koenig and Wenig,[3] Lob,[5] and Maquenne.[7]

A consideration of the quantities of the unaccounted reaction mixture (weight of the starting gases *minus* the weight of the components of residual gas computed on the basis of gas analysis, weight of formaldehyde and weight of the acid calculated as formic acid), presuming this to be the loss due to the formation of the solid products[1] on the walls of the discharge tube, shows that with increasing temperature this quantity also goes on increasing (*cf.* column 12, Table IV). But, it is, indeed, remarkable that at 80° C. this quantity is actually smaller than that at 60° C. This fact considered with a substantial increase in the yield of formaldehyde at this temperature (80° C.) suggests that the solid products might have been formed through formaldehyde which is the initial product. The higher yield of formaldehyde at 80° C. might be due to the depolymerising effect of high temperature.

It will be seen from Table I column 8 that the total quantity of the acid formed increases with the overall reaction as indicated by the volumes of gas consumed (Fig. 1, Curve 3). It is suggested that it might have been formed according to the equation $CO_2 + H_2 \rightarrow HCOOH$.[6]

In the light of the above discussion, it would appear, therefore, that in the interaction of CO and H_2 in silent electric discharge the primary reaction is $CO + H_2 \rightarrow HCHO$ (*vide supra*) which does not appear to be materially affected by a rise in temperature of the ozoniser. The results further suggest that at moderately higher temperatures the yield of formaldehyde might be actually greater due to its decreased polymerization. Further work is in progress.

Sincere thanks of the authors are due to Prof. S. S. Joshi, D.Sc. (Lond.), F.R.I.C., F.N.I., for his interest and advice.

SUMMARY

The study of the interaction of CO and H_2 under silent electric discharge yielding fairly good amounts of formaldehyde has been extended to the investigation of the influence of temperature. About 3 litres of gas mixture in the ratio $CO : H_2$ as 1 : 1 were circulated at the rate of 5 and 8 litres per minute through a Siemens' all glass ozoniser subjected to an A.C. discharge of 7·2 and 9·6 kV respectively, and 500 cycles frequency. The ozoniser was maintained at a given temperature by heating a surrounding water jacket. After six hours' exposure to discharge the washings from the absorbers were estimated for formaldehyde and acidity and the residual gas analysed with an Orsat's apparatus. Experiments were conducted at 25, 45, 60 and 80° C. Although an overall increase in the total reaction is indicated with increasing temperature, the net yield of formaldehyde, but for a slight increase at 80° C. which is perhaps due to the depolymerising effect at high temperature, is almost a constant quantity. Since very small quantities of CO_2 and unsaturated hydrocrbons are indicated in the residual gas and the proportion of $CO : H_2$ in it remains almost the same as the original one, it is concluded that formaldehyde is formed according to the reaction $CO + H_2 \rightarrow HCHO$.

REFERENCES

1.	Caress, A. and Rideal, E. K.	.. *Proc. Royal. Soc., London*, 1928, **A 120**, 370–85.
2.	Crespi, M. and Lunt, R. W.	.. *J. Chem. Soc.*, 1925, **127**, 2051.
3.	Koenig and Wenig	.. *Festschrift* 100—*Jahr. Bestehen, Tech. Hochschule Zu Karlsruher*, 1925, p. 525.
4.	Livingstone	.. *Bull. Soc. Chim., Belg.*, 1936, **45**, 334.
5.	Löb	.. *Ber.*, 1904, **37**, 3593.
6.	Losanitsch, S. M.	.. *Ibid.*, 1911, **44**, 312.
7.	Maquenne, L.	.. *Bull. Soc. Chim.*, 1883 (2), **40**, 61.
8.	Sahasrabudhey and Kalyansundaram	.. *Proc. Ind. Acad. Sci.*, 1948, **27 A**, 366.
9.	Wendt, G. L., and Evans, G. M.	.. *J. Am. Chem. Soc.*, 1928, **50**, 2610–21.
10.	Friedrich Auerbach und Werner Pluddemann	*J. Chem. Soc., Abstracts*, 1914, **1**, 488.
11.	Marek, L. F., and Hahn, D. A.	.. " The catalytic oxidation of organic compounds in the vapour phase " (1932), p. 129–35.