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Silent Electric Discharge in the Equimolar Dihydrogen-Carbon Monoxide Mixture

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Synopsis. The purpose of this paper is focused on seeking the possibility of utilizing electric discharge in H_2–CO mixtures as a mean of industrial processes. Along this line, the silent discharge in the equimolar mixture of CO and H_2 has been studied as a function of both the flow rate of reacting gas mixture and the length of the discharge tube. The yield of formaldehyde, the main product, increased with increasing flow rate of gas. At a given flow rate, however, the yield increased with increasing tube length indicating that the selectivity of formaldehyde can be increased steadily by increasing the rate of gas flow. The best value of the formaldehyde selectivity was 34% at the shortest residence time (0.25 s). Improvement of this value seems to be promising.

Although recent development of plasma chemistry[1,2] is attracting a growing attention in several special fields, the application of it for the mass production industry seems very limited. However, it is also a fact that the glow discharge has been utilized in ozone production and also in acetylene industry.[3] This shows that there still remain possibilities of utilizing the discharge reaction in some organic raw material industries. We thus attempted to study the reaction occuring in an equimolar mixture of H_2 and CO. There are several papers[4–7] which deal with the same gas system with use of various modes of discharge. Among these, Blaustein and Fu[6] showed that in a microwave discharge in static gas (H_2/CO=5) gave conversion of CO to CH_4 an C_2H_2 of approximately 17 and 22%. No yield of HCHO was reported. Quite recently, the system has been studied by Bauer[7] using several modes of glow discharge (dc, pulsed dc and rf). Reaction products seem a complex mixture and only a few compounds were analyzed quantitatively.

Experimental

An equimolar mixture of H_2–CO was used as the reactant. A 135 VA transformer provided high voltage upto 15 kV. Four discharge tubes having the same dimensions of tube diameters (o.d.=12, i.d.=10 mm) but different in tube length (2, 6, 12, and 24 cm) were used. The reactor circuit was composed of a small diaphragm pump, a rotameter and two-stage gas trap which were placed in series with the discharge tube. A gas burette, which served as the gas reservoir, was connected to the gas circuit. Of the two gas traps, one contained 150 ml of water to trap water soluble products and the other was cooled by Dry Ice–methanol mixture. Total volume of the gas circuit except the gas burette was *ca.* 840 ml. Discharge voltage was fixed at 12 kV throughout the experiments.

The product analyses were carried out separately for the gaseous products and the liquid products. Formaldehyde which was trapped in water was analyzed spectrophotometrically with use of acetylacetone and ammonium acetate. Sampling was made periodically in every 2 h. For the gaseous products, 1 ml of gas was taken with an injection syringe while for formaldehyde 10 ml of trap water was withdrawn for each time. After each time of sampling, 10 ml of fresh water was supplied to the water trap to keep the amount of trapping water constant (150 ml).

Results and Discussion

Experiments were conducted by circulating the reacting gas mixture. The gas flowing out of the discharge tube was first led to the water trap to remove the water soluble products and then to the cold trap to condense components of high boiling point. Actually, however, no detectable amount of condensate was obtained in the cold trap other than water which came from the water trap. A small amount of oily material accumulated gradually on the surface of the discharge tube.

Result of gas phase analysis is listed in Table 1. It is seen that CH_4, CO_2, and C_2H_6 are the major products in the gas phase. It is a marked contrast that no acetylene was detected in our system, while it is dominant in the discharge reaction in low pressure gases.[6,7]

The amount of HCHO trapped in water was analyzed separately. No effort was made for methanol and other alcohols which might be existed in the water trap.

General features of HCHO production can be summarized as follows.

1. In every measurement, regardless of both the tube length and flow rate, the accumulation of HCHO in water trap exhibits a downward convex curve against the reaction time, *i.e.*, the rate is rather dull at the initial stage of reaction but becomes increasingly fast with the elongation of the reaction time. This is a marked contrast to the accumulation of CH_4 in gas phase, where the amount of CH_4 increases almost linearly with the increase of reaction time.

TABLE 1. COMPOSITION OF GAS PHASE PRODUCTS

Compound	Concn/mol%
H_2	49.706
CO	39.551
Air	2.386
CO_2	3.580
CH_4	4.676
C_2H_4	0.094
C_2H_8	0.006
C_4	Trace
C_5	Trace

Tube length: 6 cm. Flow rate: 42 ml min^{-1} Discharge time: 12 h.

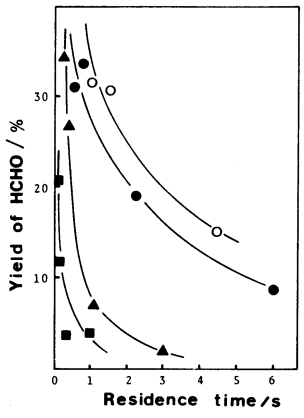

Fig. 1. Percentage yield (selectivity) of formaldehyde after 12 h of reaction as a function of the residence time. Discharge voltage: 12 kV. Curve parameter is the length of tube. ○: 24 cm, ●: 12 cm, ▲: 6 cm, ■: 2 cm.

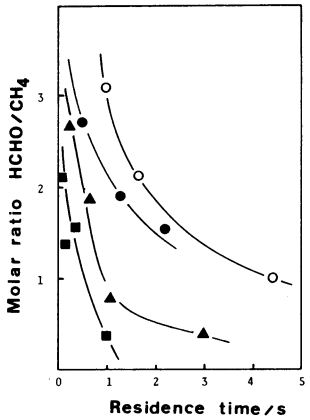

Fig. 2. Molar ratio of formaldehyde to methane against the residence time. Symbols are same as in Fig. 1.

2. The yield of HCHO increases with the increasing flow rate when the tube length is fixed. This effect is, however, only significant at the lower flow rate (*ca.* 300 ml min^{-1}) and becomes insignificant at higher rates. The effect of flow rate on the CH_4 formation seems, on the other hand, to be opposite and the lower flow rate seems to favour the production of CH_4.

3. When the flow rate is fixed, the HCHO yield increases almost linearly with increasing tube length. This applies also to the formation of CH_4.

The downward convex shape observed in the accumulation curve of HCHO seems to suggest that some sort of intermediate(s) is converted gradually to HCHO to enhance the reaction rate. On the other hand, the accumulation of CH_4, being the most dominant gaseous product, increases almost linearly with the reaction time. It is thus more likely that the accumulation of some compounds, which is rather inert against the discharge reaction than H_2 or CO themselves, will act as the energy carrier (sensitizer) as rare gas atoms do. Methane may be a candidate if this is the case.

The percentage yield of HCHO after 12 h. of the discharge reaction is plotted in Fig. 1 against the residence time (τ) of flowing gas molecule in the discharge tube. In this figure, values of percentage yield were calculated on the base of total gas volume decreased and no correction was applied for the volume occupied by gaseous products. Similarly, the molar ratio of $HCHO/CH_4$ in the reaction products is shown in Fig. 2. In these figures, lines were drawn to connect points of the same tube length. Figure 1 indicates clearly that the shorter the residence time the better the yield of HCHO, and that the increase in the tube length favours the formation of HCHO.

As has been described above, the effect of flow rate on the yield of HCHO is insensitive at higher flow rate. This indicates, at least apparently, that the use of an execessive flow rate is meaningless for increasing the yield of HCHO. However, the increase in flow rate results in the diminution of CH_4 yield reflecting upon the steep rise of the selectivity of HCHO as is seen in Figs. 1 and 2.

The rather contradicting findings with respect to the tube length and the residence time tell us that, at a given tube length, the decrease in the residence time improves the product selectivity. Note that the integrated residence time ($N\tau$, N being the number of circulation over the whole reaction time) is unchanged by the change of flow rate when the tube length is fixed. It should be also noted that, when a comparison is made at a fixed residence time, the integrated residence time increases with increasing tube length. This must increase the product yield.

Concluding Remarks

Results obtained can be summarized as follows. The main product of silent discharge reaction occuring in equimolar H_2–CO mixture at atmospheric pressure is formaldehyde, which has never been noticed in the recent works using glow discharge[7] and microwave discharge[6] conducted in low pressure gas mixtures. Although methane is found to be the second dominant product in agreement with these authors, it is contrasting that no acetylene is detectable in our experiment.

Experiments has been conducted (along the line) to increase the selective formation of formaldehyde over many by-products particularly methane. (In order to accomplish this purpose.) It was found essential to shorten the one pass-residence time. For instance, with a Siemens tube of 6 cm length the selectivity of formaldehyde increased steeply from 2.0 to 34.3% by decreasing residence time from 3.0 to 0.25 s, respectively. Corresponding to these figures, molar ratio $HCHO/CH_4$ increased from 0.22 to 2.6.

The linear velocity of flowing gas which employed in the present experiments was in the order of 24 cm s^{-1} at the highest. A hundred times greater velocity can easily be attained. If the length of discharge tube could be elongated to such a degree without purturbing the reaction conditions employed here, a very high selectivity of HCHO production is expected.

The authors are indeed grateful to the reviewer who kindly gave us notice of Bauer's work.[7]

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