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Practical Reversibility of HCN Synthesis by Electric Discharge in CH_4/N_2 Mixture

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Electric discharge in CH_4/N_2 mixture yielded HCN and H_2 as main products, accompanied by transient formation of C_2- and C_3- hydrocarbons. The practical reversibility of this HCN synthesis has been demonstrated by obtaining CH_4 and N_2 by electric discharge in HCN/H_2 mixture.

The main purpose of this work was to provide another example of reversible discharge reactions, like the previously reported CO_2 decompositon.[1] It is already known that a mixture of CH_4/N_2 is converted into HCN and H_2 by arc discharge[2] or microwave discharge.[3] HCN is also produced by the reaction of active nitrogen with hydrocarbons.[4,5] As far as we know, however, nobody has directed his attention to the backward process of these reactions. The discharge reaction in CH_4/N_2 may be stoichiometrically written as

$$2CH_4 + N_2 \longrightarrow 2HCN + 3H_2. \qquad (1)$$

Here we provide direct evidence for the reversible nature of this reaction. By term "reversible" is not meant the thermodynamic reversibility, but it simply means that the reverse reaction is not negligible.

The closed circulating reaction system used previously for CO_2 discharge decomposition was again employed in this study, with minor modifications: the system volume was variable in a range 358-558 cm^3 instead of the previous 432-632 cm^3, and the previously attached Al electrodes (6 cm apart) was replaced by stainless steel ones (2 cm apart). The high voltage needed for electric discharge was generated from the 50-cycle a-c output of a neon-sign transformer. The forward reaction was started out with a 2:1 mixture of CH_4 and N_2, and the backward reaction with a 2:3 mixture of HCN and H_2.

Figure 1 shows the discharge reaction profiles obtained with a pair of the forward (run 6) and backward (run 7) reactions conducted at almost a constant total pressure of 60 Torr (1 Torr = 133.322 Pa). Apparently, the main gaseous products in the forward reaction are HCN and H_2, and those in the backward reaction are CH_4 and N_2. This provides unequivocal evidence for the reversibility of discharge reaction (1). Furthermore, the final gas compositions of both runs

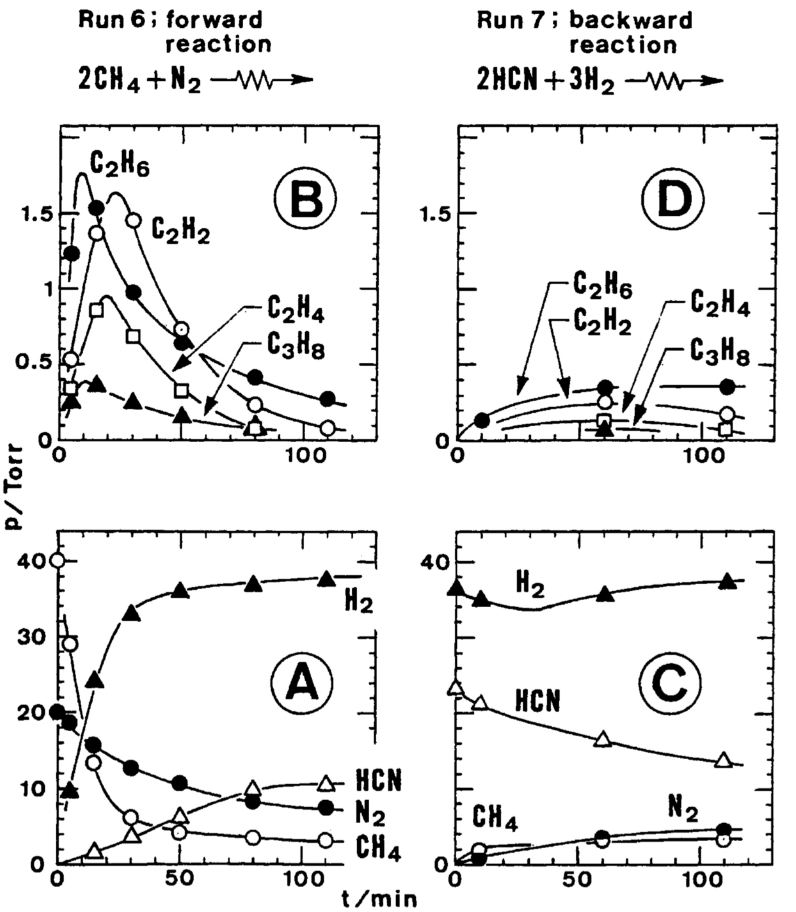

Fig. 1. Reaction profiles for reaction (1) and its reverse: partial pressures vs. discharge time. Discharge voltage and discharge current toward the end of reaction were 1560 V and 7.1 mA for run 6, and 1730 V and 7.0 mA for run 7.

are similar to each other, indicating the closeness to the equibilium composition. This reversibility was also seen when we went down to a total pressure of 30 Torr.

Two types of side reactions occur; (i) the transient formation of C_2- and C_3-hydrocarbons as shown in Figs. 1B and 1D, and (ii) the carbon deposition on the electrodes and glass walls. A small amount of hydrogen and nitrogen may be occluded in the deposited carbon. At first glance it would seem peculiar that in Fig. 1C the H_2 pressure increases slowly after a shallow minimum, but this is not unreasonable. Two factors serve to enhance the H_2 pressure. One is the H_2 release accompanying the carbon deposition from HCN. The other is artificial: the drop of the H_2 pressure due to the backward reaction is partially compensated by reducing the reaction volume so as to keep the total pressure constant.

In conclusion it is re-emphasized that little doubt is left about the reversibility of discharge reaction (1) although it is accompanied by side reactions.

References

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