Kinetics of Formation of Hydrogen Cyanide from Methane and Ammonia in a Microwave Plasma

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Abstract The reaction of CH_4 with NH_3 to produce HCN was studied at 10 and 25 torr pressure in a microwave plasma. Varying the reactant flow rate from 60 to 1050 cc./min. NTP and the microwave power from 70 to 500 watts produced conversions to HCN from 9 to 78 percent. Application of the theory of diffusion controlled discharge operation resulted in constant E/p and average electron energy at a given pressure. Combining this conclusion with the observation of invariant specific power and electron density justified replacing reaction time with specific energy in the rate equations. Mathematical models based on first order kinetics were consistent with measured reaction rates for the disappearance of CH_4 (k_1 = 0.036 liter/W-hr) and the formation of HCN (k_2 = 0.035 liter/W-hr).

Introduction One useful way to classify discharges for chemical synthesis is on the basis of the temperature ratio of the electrons to the bulk gas, T_e/T_g (Spedding, 1969). In thermal discharges, such as a high current D.C. arc or a plasma jet, T_e/T_g approaches unity, and the bulk gas temperature is usually of the order of 10,000°K. In non-thermal discharges, such as high frequency and microwave discharges at pressures below 0.5 atm., T_e/T_g may range from about 10 to nearly 100. The bulk gas temperature may be as low as 300°C (Brockmeier, 1966). Thus the non-thermal discharge provides a means for generating a significant number of high energy electrons without heating the bulk gas to a great extent. The purpose of the present study is to investigate the production of HCN under these conditions.

The microwave discharge has some definite advantages because it provides a highly reactive environment at relatively low temperature. Products that are thermally unstable can be synthesized. Reactions that have a favorable free energy change, but which normally require a catalyst or high temperature to achieve a reasonable rate, should proceed in a microwave discharge. The absence of metal electrodes aids in preventing contamination and possible undesirable catalytic effects.

Investigators have been studying the effects of microwave radiation on gases since the first generators became available about 25 years ago, but in all of these studies, except that of McCarthy (1954), there has been very little effort to measure the effects of power, flow rate, temperature, and pressure on the reaction rate in the microwave plasma. Recently, Cooper, et al. (1968), have reported a more comprehensive study of the discharge parameters that affect the chemical yield. The oxidation of HCl to chlorine was correlated as a function of the quantity $(\text{power})^{1/2}$/pressure, which was proportional to the proper variable, E/p.

The chemical reaction chosen for the present study was the following:

$$CH_4 + NH_3 \rightarrow HCN + 3\,H_2 \qquad \Delta F_{298} = +60 \text{ kcal.}$$

This reaction is not thermodynamically favorable until the temperature is raised above 900°C. The HCN is unstable below 2000°C (Sherwood and Maak, 1962). The recovery of a significant amount of HCN at the cooler temperatures (300-800°C) prevailing in a microwave reactor depends first on generating suitable activated precursors and second on these precursors combining along a reaction pathway that leads to HCN concentrations "frozen" at values greater than the equilibrium values.

This chemical reaction is particularly suitable for study in a microwave reactor. Under most conditions in the operating plasma, large concentrations of hydrogen will be present, therefore the operation can be analyzed within the framework of the diffusion-controlled theory.

Theoretical A microwave field affects only the charged particles in the reaction tube, and essentially only the electrons, because they are so much lighter than the ions present. The Boltzmann transport equation, which is an equation of continuity, represents the changes in the number and density of electrons and is the starting point for most theories of microwave discharges in a gas. These theories have been formulated by several investigators for both the initial breakdown and the steady state discharge (Rose and Brown, 1955; Brown, 1959 and 1966; Kontaratos and Demetriades, 1965). The solution to the Boltzmann equation for a steady state discharge has been discussed by Brown (1959, 1966), and an exact solution can be obtained for two limiting cases, low and high electron density.

The conditions in an operating discharge differ somewhat from the conditions at the initial breakdown. The operating discharge has a significant concentration of positive ions, somewhat greater than the electron density because the heavier ions diffuse to the walls more slowly. The electron density, n, is significantly greater than the breakdown value because of the exponential growth law for free electrons. The interaction between these charged species generates a space charge field that enhances the diffusivity of the positive ions and decreases the diffusivity of the electrons. The effect of the space charge field, E_s, is taken into account in solving the Boltzmann transport equation by superposing E_s on the microwave field:

$$E = E_s + E_p e^{j\omega t} \qquad (1)$$

At microwave frequencies the effective field for energy transfer, E_e, is substituted for the peak field in equation (1)

$$E_e^2 = E_p^2 \cdot \nu m^2/(\nu m^2 + \omega^2) \qquad (2)$$

where νm is the collision frequency for momentum transfer and ω is the radian frequency of the field ($\omega = 1.54 \times 10^{10}$ sec^{-1} at 2450 MHz). The effectiveness of energy transfer changes markedly as the relative values of νm and ω vary with pressure. If equations (1) and (2) are used to calculate the field, E, the equation of motion for an electron may be solved to get the specific power, or power input per unit volume of gas (Cooper, et al., 1968).

$$\bar{P} = ne^2E^2/(2m\nu m) \qquad (3)$$

It has been shown (Brown, 1959; MacDonald, 1966) that three proper variables are sufficient to describe breakdown conditions in electric discharges: $E\Lambda$, p^{λ}, and either E/p or $p\Lambda$. The electron density, n, must be added to this list to describe the operating discharge.

The diffusion controlled breakdown theory has been solved using the assumption of constant collision frequency ($\nu m \neq f\,[u]$) to obtain the breakdown field over a pressure range from 0.1 to 100 torr. Figure 1 shows the results of MacDonald and Brown (1949) comparing the theory with experimental results for hydrogen at 2800 MHz. Also on the same plot are the curves for steady operating conditions, where n_o is the electron density at the centerline of the tube. Similar curves have been reported by others using air (Rose and Brown, 1957) and helium (Reder and Brown, 1954). Figure 1 indicates that $E/p \approx 10$ for pressures above 10 torr. Another important observation is that if $n_o > 10^9$ cm^{-3}, E is practically constant as n_o is increased. It can be shown (Cooper, et al., 1968) that the average electron energy,

u, is determined by E/p, so the value of u is also steady at the above conditions. Since the rate of formation of excited species is determined by E/p, the distribution of these reactive species will also be practically constant at a given pressure if $n_o > 109$ cm^{-3}. The electron density in the present system is estimated as at least 10^{10} cm^{-3}.

For certain reactor and waveguide geometries, and especially that used in this work, one effect of increasing the incident power is to extend the electric field farther outside the waveguide into the flowing gas. The region in which the electric field is strong enough to sustain a discharge is the same as the extent of the visible glow. At constant pressure the length or volume of the visible discharge may be directly proportional to the power absorbed in the microwave reactor, especially at low to moderate power levels. In the linear region, the reciprocal of the slope is the specific power, or power absorbed per unit volume, which is a constant.

Equation (3) shows the relationship between the specific power and electron density. It has been shown above that, at constant pressure in the high electron density limit, the values of E and vm will be steady. Therefore, the electron density will be constant if the specific power remains constant over this range of conditions. This implies that over a moderate range of power levels, the result of increasing the power is simply to lengthen the microwave reactor, without causing any significant change in the average electron energy, the electron density, or the kinds of reactions occurring. The longer reaction zone has the same environment as at lower powers, and the contact time is increased proportionately with the power.

Experimental The apparatus used for this study is shown schematically in Figure 2. The microwave power was supplied by an Eimac PPS-2.5A Power Pack at a fixed frequency of 2450 MHz using a continuous wave magnetron with an output adjustable between 200 and 2500 watts. A crescent-shaped variable attenuator was installed in the waveguide to permit operation below 200 watts. An impedance meter consisting of a movable probe in a slotted waveguide was used to measure the voltage standing wave ratio (VSWR). The power incident on the reactor was detected with a loop-type directional coupler and read on a microwave power meter. The power actually absorbed in the discharge region was calculated from the incident power reading and the VSWR. A tapered waveguide section with a slot for the reactor coupled the power into the plasma (Fehsenfeld, et al., 1965).

The microwave reactor was a 13 mm. OD quartz tube. A Liebig condenser was mounted around it to permit cooling the tube with a high-velocity air stream. A fitting in the exhaust end of the tube was used to install a chromel-alumel thermocouple in a thin-walled quartz shield for those runs in which temperatures were measured.

Research grade methane and ammonia were used as feed gases without further purification. Each feed rate was measured at atmospheric pressure with a Matheson No. 600 series rotameter. An evacuated glass bulb was used to obtain a sample for gas chromatography using a hydrogen flame detector. In addition, a condensed sample was obtained by operating the three toggle valves to direct the product stream through a glass trap cooled with liquid nitrogen. The condensed products were dissolved in water and titrated for cyanide and ammonia.

Results Experimental results were obtained over the following ranges of operating conditions: gas pressures from 10 to 25 torr, absorbed powers from 70 to 500 watts, and gas feed rates from 60 to 1050 cc./min. measured at NTP, that is, 21°C and atmospheric pressure. For most of the runs, the feed ratio of methane to ammonia was 1:2. The use of this feed ratio rendered methane the limiting component for the formation of HCN in all of the experiments. The major products from the reactor were HCN, hydrogen, and nitrogen. In addition, there was a minor amount of

acetylene, and very small quantities of ethane, ethylene, and other hydrocarbons.

In many studies of reaction kinetics in electric discharges, the specific energy, U/V, has been used rather than reaction time, t, to correlate the results (Vasil'ev, et al., 1937; Borisova and Eremin, 1967). This has also been done here, for reasons explained in the theory section and because calculation of specific energy from the measured power and feed rates was more accurate than calculation of space time.

The results of chemical analyses are shown in the following figures. The disappearance of methane followed an apparent first-order kinetic expression at 10 torr, Figure 3. The rate constant for methane decomposition was 3.6×10^{-2} liters/W-hr. At 25 torr, the measured rate constant equalled that at 10 torr.

Figure 4 depicts the production of HCN as a function of specific energy at 10 torr. At low U/V (< 18 W-hr/l) this figure exhibits a linear relationship with an initial slope practically the same as the slope of the line in Figure 3 for methane decomposition. At higher U/V the line curves, approaching asymptotically a value of approximately 80 percent conversion of methane to HCN for a U/V greater than 80 W-hr/l. Experiments at 10 and 25 torr pressure yielded essentially the same results, just as in the case of the methane decomposition.

At higher specific energies (> 40 W-hr/l), very small amounts of an as yet unidentified dark brown solid were produced.

In a separate series of experiments, the axial temperature profiles were measured just below and part-way into the exhaust end of the operating discharge. At 10 torr, the absolute temperature increased about 10 percent as the power was increased nearly fourfold. The conclusion is that large variations in power cause only minor changes in the temperature profiles in the discharge. For each profile, the temperature near the center of the glowing plasma was 1000°C. The higher the gas rate, the higher the temperature is at the edge of the glow: as the flow rate was increased from 60 to 180 to 900 cc./min., the respective temperatures were 250, 350, and about 500°C.

The energy requirement per gram of HCN was calculated at different values of specific energy. The minimum energy requirement was 70 W-hr/gm. of HCN at a specific energy of 4.6 W-hr/l, corresponding to a 17 percent conversion to HCN.

Discussion The correlation of results by means of a straight line in Figure 3 indicates that the decomposition of methane in a microwave plasma can be described by a first-order reaction rate expression at 10 torr:

$$\ln (1 - X_A) = -k_1 (U/V) \qquad (4)$$

Because of the first order expression, no volumetric expansion factor is required.

The decomposition of methane in the presence of ammonia in a microwave plasma leads to the formation of HCN by a series of at least two elementary reactions. In a series mechanism, the formation rate for the product is controlled by the rate of the slowest reaction in the series. The HCN will also be decomposed by exposure to the discharge. The series of reactions forming HCN will be summarized by $A \rightarrow R$ and the decomposition of HCN will be abbreviated to a single reaction $R \rightarrow S$, so that

$$A \xrightarrow{k_2} R \xrightarrow{k_3} S \qquad (5)$$

The form of equation (5) implies that only first-order reactions are considered in this mechanism. The corresponding integrated rate expression becomes

$$\frac{N_R}{N_{A_o}} = \frac{k_2}{k_2 - k_3} \left[1 - \exp \left[- (k_2 - k_3) U/V \right] \right] \exp (-k_3 U/V) \qquad (6)$$

where U/V has replaced time, and N_{A_o} is the molar feed rate of methane.

Equation (6) is the mathematical model that was used to generate the curve shown in Figure 4. This model gives a nearly straight-line correlation at low U/V, which begins to curve significantly at about 30 W-hr/l as the HCN begins to react to a large extent. However, the HCN is quite stable, since 80 percent conversion to HCN can be achieved, indicating that k_3 is small. If $k_3 << k_2$, equation (6) may be simplified to

$$N_R/N_{A_o} = \left[1 - \exp(-k_2U/V)\right] \exp(-k_3U/V) \qquad (7)$$

The values of k_2 and k_3 at 10 torr were calculated by determining the best fit to the experimental data in Figure 4. The same procedure was used for data at 25 torr. The results are shown in Table I.

Table I

Rate Constants Calculated from Equation (6)

Pressure, torr	k_2, l./W-hr	k_3, l./W-hr
10	3.5×10^{-2}	3.65×10^{-3}
25	3.5×10^{-2}	3.65×10^{-3}

Since k_3 is an order of magnitude smaller than k_2, equation (7) is an accurate approximation to the kinetic model. Note that for low values of U/V, the exponential containing k_3 is practically unity wherefore equation (7) reduces to equation (4), which describes the methane decomposition. In the limit of zero conversion, at zero U/V, the rate of formation of HCN is identical to the methane decomposition rate. The value for k_1 calculated from Figure 3 agrees with the initial slope of Figure 4 (k_2) to within 5 percent. Therefore, the decomposition of methane appears to be the rate-controlling step in the formation of HCN, with the result that k_2 equals k_1. This model is consistent with the experimental results up to about U/V = 60 W-hr/l at both 10 and 25 torr.

At specific energies greater than 60 W-hr/l, no model has been found to describe the results. The products from the HCN decomposition (S) probably tend to reform some HCN.

Nomenclature

A = methane
E = electric field strength, volts/cm.
E_e = effective field strength, volts/cm.
E_p = amplitude of electric field, volts/cm.
E_s = space charge electric field, volts/cm.
e = electronic charge, coulomb.
k_1 = rate constant for decomposition of methane, 1/w-hr.
k_2 = rate constant for formation of hydrogen cyanide, 1/w-hr.
k_3 = rate constant for the decomposition of hydrogen cyanide, 1/w-hr.
m = electron mass, gram.
N = moles of chemical compound, moles
n = electron density, cc^{-1}
n_o = centerline electron density, cc^{-1}
P = specific power, watts/cc.
p = pressure, torr.
R = hydrogen cyanide
S = decomposition products of hydrogen cyanide
T_e = electron temperature, °K
T_g = gas temperature, °K
t = reaction time, min.
U = absorbed power, Watts
u = average electron energy, electron volts
V = feed rate, cc/min at 21°C and 760 mm Hg.
VSWR = voltage standing wave ratio
X_A = fractional conversion of methane
Λ = characteristic diffusion length, cm.

λ = free space wavelength, cm.
ν_m = collision frequency for momentum transfer, sec^{-1}.
ω = radian frequency of field, sec^{-1}.

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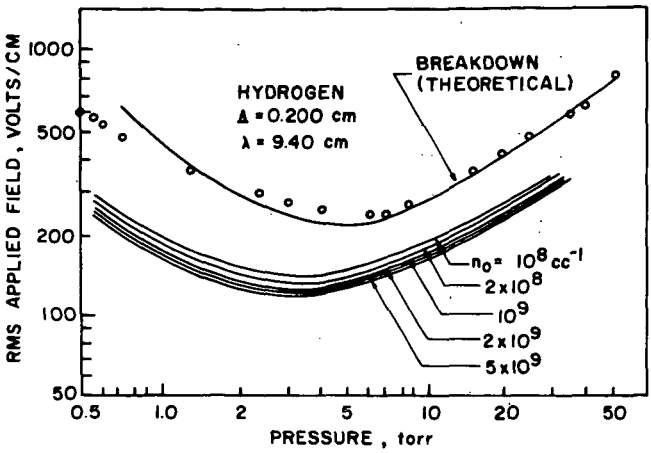

FIGURE 1. EXPERIMENTAL CURVES FOR STEADY-STATE MICROWAVE DISCHARGES.

o : EXPERIMENTAL DATA

FROM : MACDONALD AND BROWN, 1949

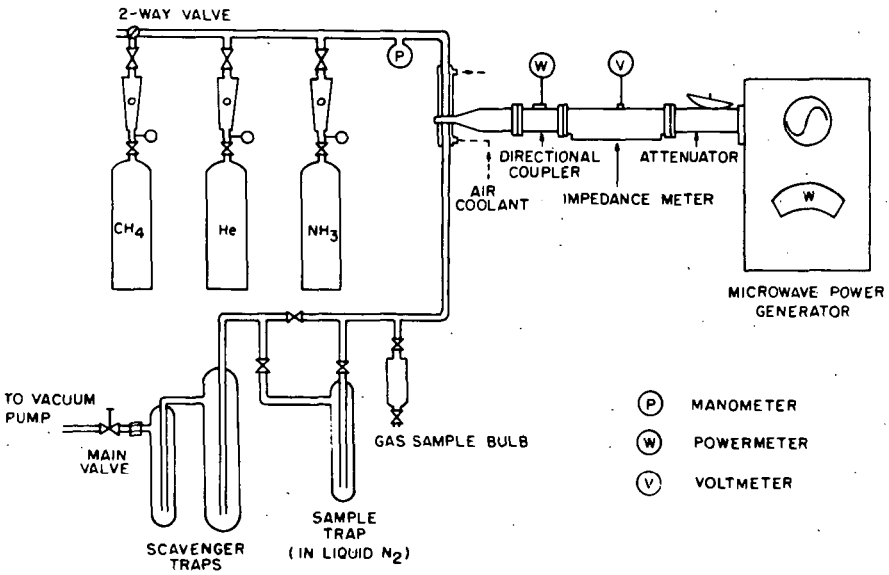

FIGURE 2. SCHEMATIC DIAGRAM OF APPARATUS.

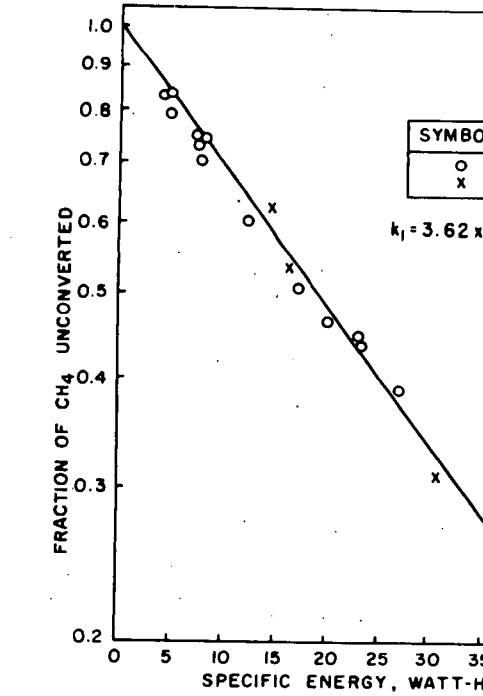

FIGURE 3. EFFECT OF SPECIFIC MICROWAVE ENERGY ON THE DECOMPOSITION OF CH_4 AT 10 torr PRESSURE.

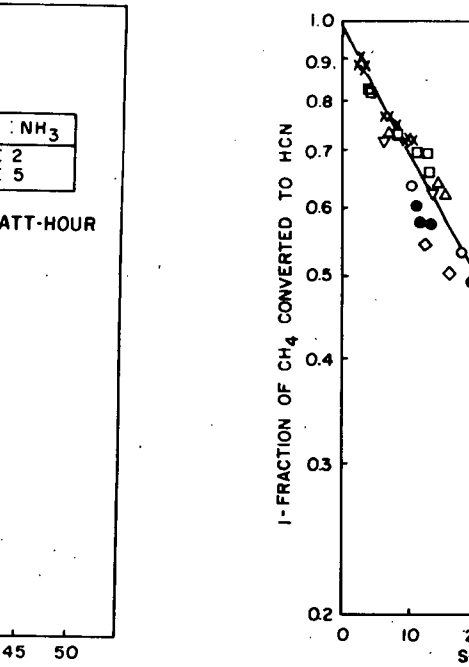

FIGURE 4. EFFECT OF SPECIFIC MICROWAVE ENERGY ON THE FORMATION OF HCN AT 10 torr PRESSURE.