RADICAL - MOLECULE AND ION - MOLECULE REACTIONS IN A MONOSILANE - ETHYLENE PLASMA.

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ABSTRACT

This paper reports on a mass spectrometric study of the neutral and ionic species in a low pressure R.F. discharge sustained in a C_2H_4 - SiH_4 mixture diluted in helium.

It is shown that C_2H_4 is readily decomposed into $C_2H_2{}^*$ and that the formation of crossed neutral and ionic products results from radical-radical, radical - molecule or ion-molecule reactions.

1. INTRODUCTION

The chemical reactions which occur in various hydrocarbon gas (CH_4, C_2H_4, C_2H_2 ...) submitted to U.V. light, electron impact or an electric discharge have already been extensively investigated (1) (2) (3). Photolysis and radiolysis in pure SiH_4 received also a great deal of attention (4).

We have recently reported the results of mass spectrometric studies of R.F. discharges in silane (5) (6) and methane-silane mixtures (7).

The present paper is a part of our ongoing studies of the chemistry of R.F. discharges in reactive gases and it reports on a mass spectrometric study of the ionic and neutral species present in a C_2H_4 - SiH_4 plasma.

2. EXPERIMENTAL

The experimental apparatus used in this work has been described in a previous paper (5). The gas is sampled from the discharge through an orifice of diameter 200 µm bored in the wall.

The neutral and ionic species are measured by means of a quadrupole mass spectrometer. The total gas pressure may be set between 0.1 and 1 torr, and the C_2H_4 and SiH_4 gases are diluted in helium at concentration of 5 %.
The relative concentration of C_2H_4 and SiH_4 in the vessel is defined by

$$g = \frac{F_{SiH_4}}{F_{SiH_4} + \frac{1}{2} F_{C_2H_4}}$$

where F_{SiH_4} and $F_{C_2H_4}$ are the inlet flow rates of the gases. The maximum of the total flow rate is 42 cm³/min (S.T.P.).

3. RESULTS

Dissociation of gases in the discharge

The fig. 1 shows the evolution of the concentrations of the primary gases as a function of the R.F. power applied to the discharge. The concentrations are represented by the ratio I^+/I_o where I^+ is the intensity of the ion currents for selected masses when the discharge is on and I_0 this intensity when the discharge is off.

It can be seen that C_2H_4 is strongly dissociated in the discharge : for an R.F. power of 25 W about 90 % of C_2H_4 and 75 % of SiH_4 are dissociated. This strong decomposition results in part from the dilution of the gases and, as we shall see below, plays an important role in the chemistry of the discharge.

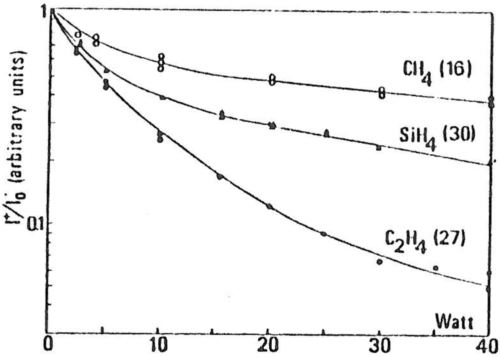

Fig. 1 : Decomposition of the primary gases as a function of the discharge power.

Neutral species

We have reported in table 1 the neutral species observed in C_2H_4 - SiH_4 - He discharges (5 W, 1 torr, 42 cm³/min S.T.P.).

Hydrocarbons	CH_4, C_2H_6, C_3H_4, C_3H_6, C_4H_2, C_4H_4, C_4H_6, C_4H_8, C_4H_{10}
Higher silanes	Si_2H_6 (disilane)
crossed products	CH_3SiH_3 (methylsilane) $C_2H_5SiH_3$ (ethylsilane)

Table 1 : Neutral products .

Hydrogen has not been reported in this table but it is obviously present in the discharge.

It is not possible to obtain a direct evidence of the formation of C_2H_2 because of mass interferences between the fragmentation patterns of C_2H_2 and C_2H_4 , but as we shall see in the discussion the formation of C_4H_2 and C_4H_4 implies the existence of C_2H_2.

The crossed products have been identified as methylsilane (CH_3SiH_3) and ethylsilane ($C_2H_5SiH_3$) . The formation of these gases has also been observed in radiolysis of C_2H_4 - SiH_4 mixtures (8).

The fig. 2 gives the concentrations of some of the major neutral products relative to the initial concentration of C_2H_4 + SiH_4 as a function of the gas phase composition g. The total concentration of the C_3 + C_4 hydrocarbons is relatively important (up to 6,5 %) and the concentrations of Si_2H_6 and crossed products (CH_3SiH_3 + $C_2H_5SiH_3$) slightly lower (respectively 1,5 % and 0,5 %).

Positive ions

A part from the helium and hydrogen ions the major carbon, silicon and crossed ions have been reported in table 2.

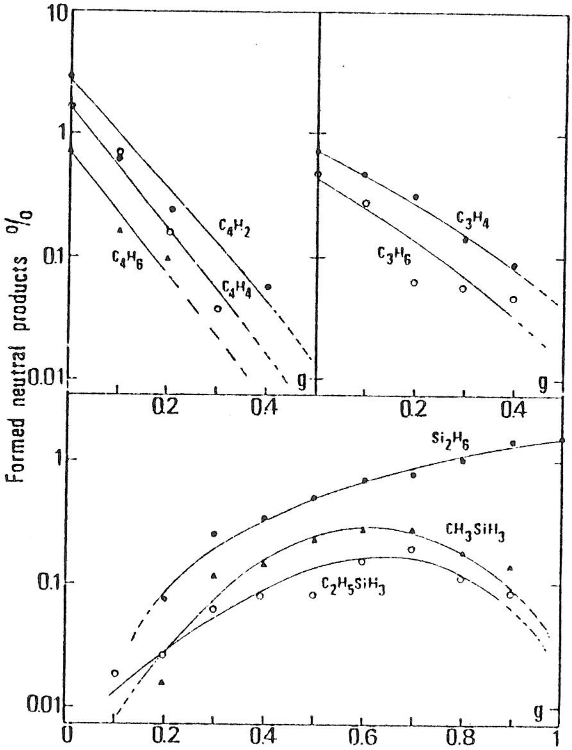

Fig. 2 : Fractions of neutral products relative to the initial concentration of gases as a function of the gas phase composition (1 torr, 5 W, 42 cm³/min).

Hydrocarbons	C_1	CH^+ (13), CH_2^+ (14), CH_3^+ (15), CH_4^+ (16)
	C_2	$C_2H_2^+$ (26), $C_2H_3^+$ (27), $C_2H_4^+$ (28), $C_2H_5^+$ (29)
	C_3	$C_3H_3^+$ (39), $C_3H_5^+$ (41)
	C_4	$C_4H_2^+$ (50) $C_4H_3^+$ (51), $C_4H_4^+$ (52), $C_4H_5^+$ (53)
silane ions	Si_1	SiH^+ (29), SiH_2^+ (30), SiH_3^+ (31)
	Si_2	Si_2H^+ (57), $Si_2H_2^+$ (58), $Si_2H_3^+$ (59), $Si_2H_4^+$ (60), $Si_2H_5^+$ (61)
crossed ions	SiC	$SiCH_3^+$ (43), $SiCH_4^+$ (44), $SiCH_5^+$ (45)
	SiC_2	$SiC_2H_3^+$ (55), $SiC_2H_5^+$ (57), $SiC_2H_6^+$ (58), $SiC_2H_7^+$ (59)

Table 2 : Positive ions of the C_2H_4 - SiH_4 - He discharge.

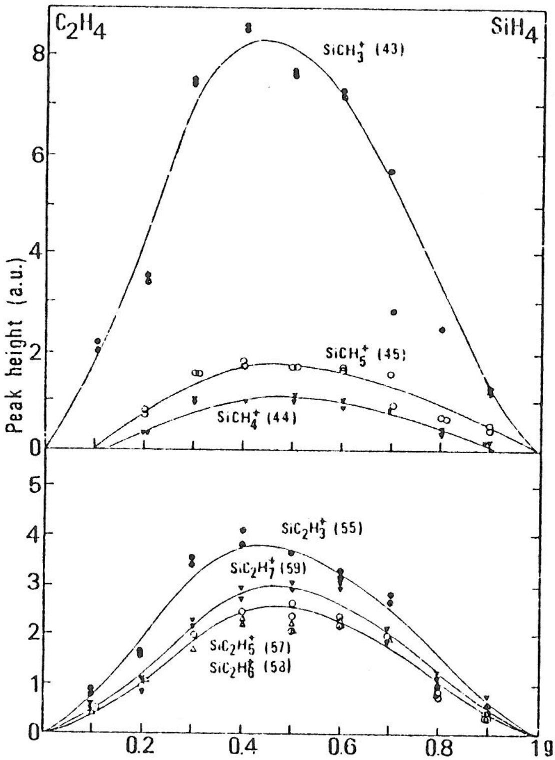

Fig. 3 : Absolute intensities of crossed ions as a function of the gas phase composition (0.15 torr, 50 W, 42 cm³/min).

The relative abundances of these various ions are entirely different from those obtained by electron impact ionization of the neutral products. For example if we compare the observed repartition of crossed ions in the discharge (Fig. 3) with the fragmentation pattern by electron impact of CH_3SiH_3 and $C_2H_5SiH_3$ there is a complete disparity :

the fragmentation pattern of CH_3SiH_3 will give $SiCH_4^+$ (44) and $SiCH_5^+$ (45) as major ions and for $C_2H_5SiH_3$ one would observed $SiC_2H_8^+$ (A.P. 10.8 eV) which is not detected in the discharge.

4. DISCUSSION

The first point to be emphasize is the disagreement between the neutral products observed in our discharge and those observed either in photolyses and discharges in C_2H_4 (1) (2). On the other hand R F discharges in C_2H_2 lead to the formation of substantial amounts of C_4H_2 (3). Furthermore the major ionic product from electron impact on C_2H_4 is $C_2H_2^+$. It is thus reasonable to suppose that the strong decomposition of C_2H_4 in our discharge leads to the formation of acetylene C_2H_2 (9) according to the following reaction :

$$e + C_2H_4 \longrightarrow C_2H_2^* + H_2 \text{ (or 2H)} + e$$

The $C_2H_2^*$ formed may be vibrationnally excited.

Another source of destruction of C_2H_4 is the reaction of H atoms :

$$H + C_2H_4 \longrightarrow C_2H_5^* \xrightarrow{M} C_2H_5 \quad (k = 1.8\ 10^{-13}\ cm^3/mol.s)$$

The formation of C_4H_2 may be accounted for as being due to further reactions of $C_2H_2^*$:

$$C_2H_2^* + C_2H_2 \longrightarrow C_4H_2 + H_2$$

It is also known that the main radicals formed in a SiH_4 plasma are SiH_2 and SiH_3 (5) (6). Thus the observed crossed products must be the results of reactions between hydrocarbon radicals and silane radicals :

$$C_2H_5 + SiH_3 \longrightarrow C_2H_5SiH_3$$

We have also shown that the observed ions are not representative of the fragmentation of neutrals by electron impact. A comparison of our experimental results with the repartition of ions obtained by high pressure mass spectrometry and tandem mass spectrometry in mixture of C_2H_4 and C_2H_2 with SiH_4 (10) (11) leads us to assume that these ions are formed through ion-molecule reactions, most of these reactions leading to the formation of $SiCH_3^+$ and $SiC_2H_3^+$ which are the major crossed ions observed in the discharge. The most important reactions are :

$$SiH_2^+ + C_2H_4 \longrightarrow SiCH_3^+ + CH_3 \quad (k = 4{,}8\ 10^{-10} cm^3\ mol^{-1}\ s^{-1})$$

$$C_2H_2^+ + SiH_4 \longrightarrow SiCH_3^+ + CH_3 \quad (k = 0{,}2\ 10^{-10} cm^3\ mol^{-1}\ s^{-1})$$

$$SiH_2^+ + C_2H_4 \longrightarrow SiC_2H_3^+ + H_2 + H \quad (k = 2{,}6\ 10^{-10} cm^3\ mol^{-1}\ s^{-1})$$

$$C_2H_2^+ + SiH_4 \longrightarrow SiC_2H_3^+ + H_2 + H \quad (k = 3{,}5\ 10^{-10} cm^3\ mol^{-1}\ s^{-1})$$

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