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The Role of Halogens in the Plasma Polymerization of Hydrocarbons

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ABSTRACT

Vinyl chloride, vinyl fluoride, and tetrafluoroethylene were polymerized in a radio frequency electric glow discharge. It was found that when compared with the unhalogenated simple hydrocarbons, the rates of polymer deposition are in the order vinyl chloride, acetylene, tetrafluoroethylene, vinyl fluoride, ethylene. This observation can be rationalized by considering the ease with which free radical and unsaturated species can be formed in the plasma. IR spectra show that the structures of plasma-polymerized vinyl chloride and vinyl fluoride are in many respects similar to the plasma-polymerized hydrocarbon. The spectrum of plasma-polymerized tetrafluoroethylene, however, does not resemble that of conventional polytetrafluoroethylene. Addition of dichlorodifluoromethane to the monomer stream dramatically increased the polymer deposition rate; the effect is more subdued for chloromethane and is negligible for tetrafluoromethane. Elemental analysis indicates that little of the added halogens is present in the resultant polymers. Thus the halogenated compounds appear to act as a gas phase catalyst for the plasma polymerization of hydrocarbons.

INTRODUCTION

Although the polymerization of organic and organometallic compounds in low-pressure electric discharges has been known for some time, there is at present insufficient detailed knowledge to permit a complete description of the polymerization reaction. The main difficulty lies in the complexity of the process. In the plasma created by a discharge, there are ions, excited molecules, and free radicals as well as undissociated monomer molecules. Relative concentrations of these species vary not only with the nature of the monomer, but the specific conditions of the discharge as well. Nevertheless, there is now enough understanding of the basic characteristics of plasmas of simple gases to permit us to propose possible mechanisms for the polymerization of more complex molecules. In a recent series of papers from this laboratory, we have reported on such studies for the plasma polymerizations of saturated and unsaturated hydrocarbons [1-3].

The present work extends our previous studies to the plasma polymerization of halogenated hydrocarbons and the effect of halogen-containing compounds on the plasma polymerization of hydrocarbons. Previously Westwood [4, 5] and Brown [6] studied the general features of the plasma polymerization of halogenated vinyl monomers. Hays [7] and Brown [6] have shown that the addition of halogens produced a modest enhancement of the rate of polymerization of styrene and methyl methacrylate. The purpose of our paper is to further elucidate the possible mechanism in the polymerization processes carried out in a radio frequency glow discharge.

EXPERIMENTAL DETAILS

The experimental apparatus used for this work was identical to that described previously [1].

The discharge was sustained in a glass bell jar containing two parallel disk electrodes over which a piece of aluminum foil was placed to collect the deposited polymer. The diameter of these copper electrodes was 6 in. and the distance between them was adjusted to 5 cm. Power for the discharge was supplied by an IPC Model PM401 generator which operates at 13.56 MHz and has maximum output of 150 W. The upper electrode was connected to the generator through an impedance matching network while the lower electrode was grounded and water cooled.

The monomer flow was controlled by a needle valve and was introduced at a point above the upper electrode. The flow rate of monomer was measured with a rotameter. The gas pressure in the reactor was determined by a McLeod gauge and was adjusted by a valve between the reactor and the vacuum pump. Monomer gases were purchased from Matheson Gas Products and were used as received. The rate of polymer deposition was determined by weighing the amount of polymer accumulated on a piece of aluminum foil covering the lower electrode.

RESULTS AND DISCUSSION

Polymerization of Vinyl Chloride and Vinyl Fluoride

Figure 1 shows the polymer deposition rates when vinyl chloride and vinyl fluoride are polymerized at a pressure of 0.5 Torr and a power of 50 W. Data for ethylene and acetylene have also been included in Fig. 1 for the sake of comparison. The order of the polymer deposition rates is $C_2H_3Cl > C_2H_2 > C_2H_3F \gg C_2H_4$. If the data are represented in terms of percent of monomer fed converted to polymer

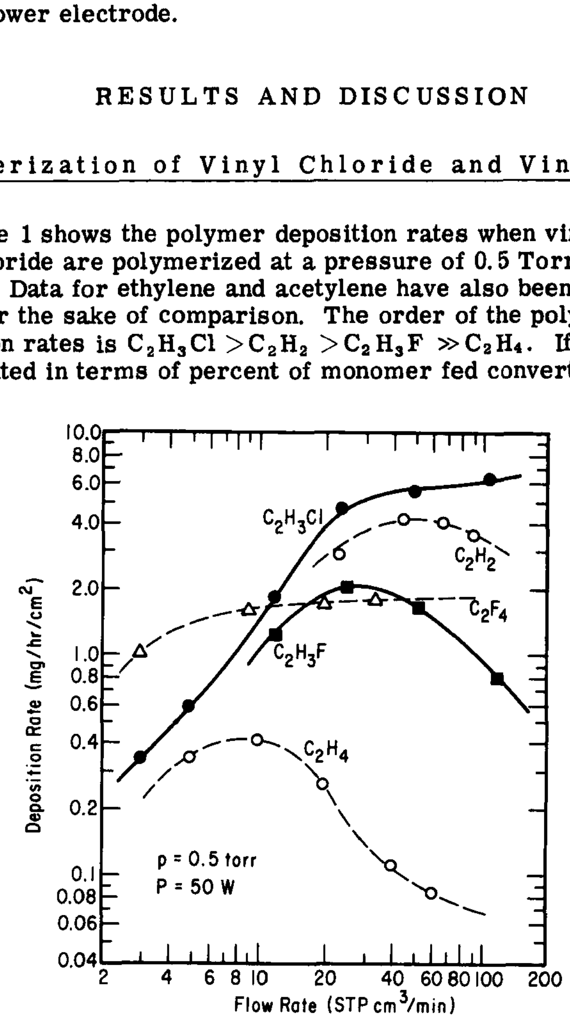

FIG. 1. Polymer deposition rates on a weight basis for various monomers.

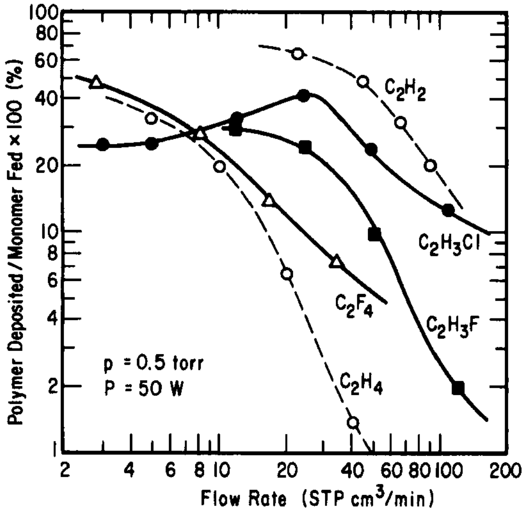

FIG. 2. Polymer deposition rates in terms of percent of monomer fed converted to polymer deposited for various monomers.

(see Fig. 2), the order of C_2H_3Cl and C_2H_2 is reversed. It should be noted in Fig. 1 that in each case the rate of polymer deposition passes through a maximum with increasing monomer flow rate, and that the flow rate producing a maximum deposition rate is shifted upscale with increasing ease of polymerization. These two effects have been noted previously in a comparison of the rates of hydrocarbon polymerization [3], and a tentative explanation for the shape of the deposition rate vs flow rate curve has been proposed [2].

The form of the polymers obtained for the conditions shown in Fig. 1 strongly depends on the nature of the monomer and the monomer flow rate. Thus ethylene produces a powder and a film at low flow rates and a film at high flow rates while acetylene forms only a powder under all conditions obtained with the existing equipment [1-3]. Vinyl chloride produces a film and a small amount of powder at low flow rates and only a powder at high flow rates. Vinyl fluoride is similar to vinyl chloride except that the rate of powder formation is significantly reduced at higher flow rates.

Figure 3 shows the IR spectra of the polymeric powder obtained from vinyl chloride, vinyl fluoride, and acetylene. All three spectra bear an obvious resemblance to each other. The peak at 1600 cm^{-1} (C=C bonds) indicates a high degree of unsaturation in each of the polymers. The bonds at 1700 cm^{-1} (C=O bonds) and 3400 cm^{-1} (OH bonds) suggest that all three polymers are

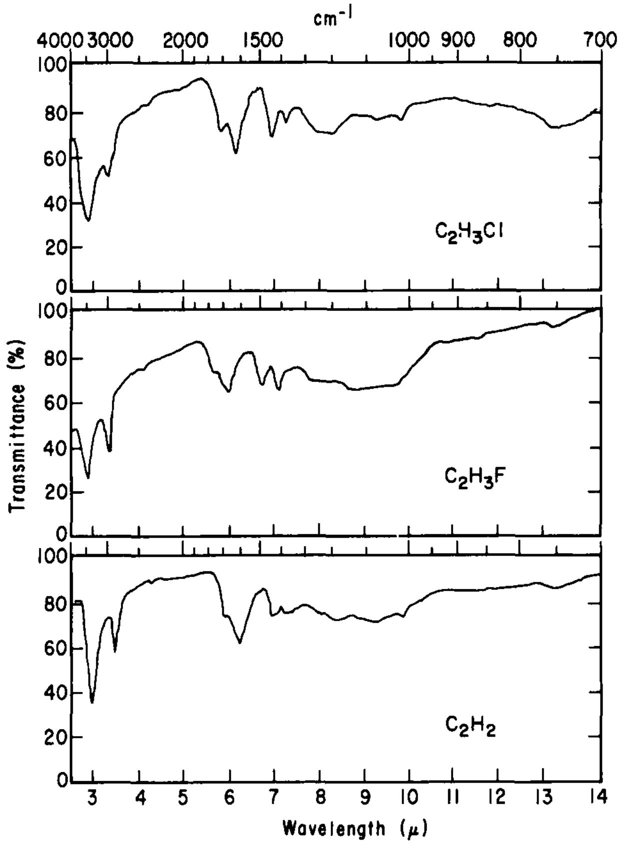

FIG. 3. Infrared spectra of plasma polymerized powders obtained from C_2H_3Cl, C_2H_3F, and C_2H_2.

oxidized to some degree. It is believed that this oxidation occurs once the polymer is removed from the discharge and is exposed to air [2]. The peaks at 2960 cm^{-1} (CH_2 stretch), 1463 cm^{-1} (CH_2 bending), and 1369 cm^{-1} (CH_3 bending) reflect the hydrocarbon nature of these polymers. The absence of the doublet near 730 cm^{-1}, which is characteristic of crystalline hydrocarbons, shows that the polymers are amorphous [1]. The broad peak near 750 cm^{-1} (C—Cl stretch) for the vinyl chloride polymer and the peak at 1000-1100 cm^{-1} (C—F stretch) for the vinyl fluoride polymer are the only characteristics which distinguish these materials from that derived from acetylene.

From elemental analysis the stochiometry of the polymer produced from vinyl chloride was established to be $C_2H_{2.0}Cl_{0.7}$. This stochiometry is to be compared with that for polymers obtained from ethylene ($C_2H_{2.7}$) and acetylene ($C_2H_{1.9}$).

While it is not possible to postulate a comprehensive mechanism for the plasma-polymerization of vinyl chloride and vinyl fluoride, an explanation can be offered to interpret the relative polymer deposition rates observed in Fig. 1. As discussed previously [2, 3], we believe that the process of plasma polymerization occurs via a free radical mechanism which is initiated by collisions between free electrons and monomer molecules. Furthermore it has been tentatively established [3] that the formation of acetylene and its subsequent participation as a derivative monomer are important steps of the polymerization mechanism. In view of this mechanism, two factors contribute to high rates of polymer formation: high concentrations of free radicals and the presence of unsaturation in the monomer structure. The dominant role of free radicals, rather than ions, as reactive species has been discussed previously [3].

For the vinyl compounds investigated here, the following reactions are assumed to be the initial steps of the mechanism [8, 9].

$$e + C_2H_4 \rightarrow C_2H_2 + H_2 + e, \quad \Delta H = 41.7 \text{ kcal/mole} \quad (1)$$

$$\rightarrow C_2H_2 + 2H\cdot + e, \quad \Delta H = 145.0 \text{ kcal/mole} \quad (1a)$$

$$e + C_2H_3Cl \rightarrow C_2H_2 + HCl + e, \quad \Delta H = 24.6 \text{ kcal/mole} \quad (2)$$

$$\rightarrow C_2H_2 + H\cdot + Cl\cdot + e, \quad \Delta H = 127.8 \text{ kcal/mole} \quad (2a)$$

$$e + C_2H_3F \rightarrow C_2H_2 + HF + e, \quad \Delta H = 18.2 \pm 2 \text{ kcal/mole} \quad (3)$$

$$\rightarrow C_2H_2 + H\cdot + F\cdot + e, \quad \Delta H = 152.6 \pm 2 \text{ kcal/mole} \quad (3a)$$

The relative ease with which Reactions (1) through (3a) proceed should depend principally on the activation energy associated with each reaction. For electron-molecule collisions these activation energies are coincident with the energy required to raise the molecule to an antibonding state which would permit dissociation. Since this state is achieved through an electronic transition of the molecule, the corresponding activation will not be the same as the thermal, or unimolecular, activation energy.

Unfortunately the true activation energies required for Reactions (1) through (3a) are not known. Nevertheless we might crudely estimate their relative magnitudes by examining the appropriate heats of reaction. This approach, while lacking adequate theoretical support, has been found to be correct empirically in many instances [10]. It is for this reason that we have identified the heat of reaction for each process taken from the literature [11].

The heats of reaction associated with Reactions (2) through (3a) suggest that vinyl fluoride will dissociate somewhat more readily than vinyl chloride to form acetylene and the corresponding hydrogen halide via Reactions (2) and (3). The opposite order is expected if Reactions (2a) and (3a) are considered. Thus while both monomers readily produce acetylene, a very active derivative monomer, vinyl chloride should produce free radicals more readily than vinyl fluoride. Since the presence of free radicals is essential to the propagation process, these arguements could explain why vinyl chloride polymerizes more rapidly than vinyl fluoride.

The dissociation of ethylene via Reaction (1) requires considerably more energy than do similar processes involving vinyl chloride or vinyl fluoride. On the other hand, the dissociation of ethylene via Reaction (1a) requires more energy than Reaction (2a) but less energy than Reaction (3a). In view of these orderings we may conclude that the formation of acetylene and free radicals from ethylene are both relatively slow processes, and that it is for these reasons that ethylene polymerizes more slowly than either vinyl chloride or vinyl fluoride.

An additional reason for the higher rates of polymer deposition observed for halogen-containing monomers is the ease with which free halogen atoms, produced by dissociation of the monomer [12, 13], can participate in the abstraction of hydrogen atoms via reactions such as

$$X\cdot + RH \rightarrow R\cdot + HX \qquad (4)$$

The activation energies for these processes are substantially lower than for similar processes involving hydrogen atoms:

$$H\cdot + RH \rightarrow R\cdot + H_2 \qquad (5)$$

Further discussion of Reactions (4) and (5) will be presented in connection with the rate of halogenated additives in the polymerization of hydrocarbons.

Polymerization of Tetrafluoroethylene

Tetrafluoroethylene (TFE) polymerizes more rapidly than ethylene as shown in Fig. 1. However, if they are compared in terms of the fraction of monomer converted to polymer (see Fig. 2), their rates are almost comparable except at higher flow rates where TFE polymerizes more rapidly by a substantial degree. The appearance of the polymer deposited from TFE is a smooth, rigid, slightly yellowish and transparent film throughout the entire range of flow rate. This appearance is in contrast with many gaseous unsaturated monomers, i.e., ethylene, propylene, vinyl chloride, and vinyl fluoride, which show powder formation along with film formation at low flow rates.

The effects of power and pressure on the polymer deposition rate are shown in Figs. 4 and 5. The observed trends are qualitatively the same as those for ethylene [2]. Operation at pressures above 0.7 to 0.8 Torr was found to be difficult due to a contraction of the glow so that it no longer fully covered the electrode surfaces.

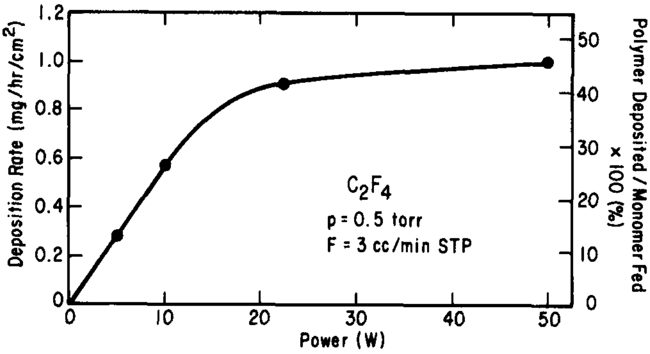

FIG. 4. The effect of discharge power on the deposition rate of tetrafluoroethylene.

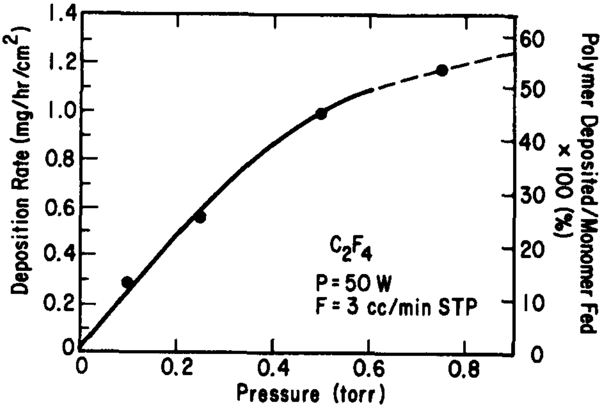

FIG. 5. The effect of pressure on the deposition rate of tetrafluoroethylene.

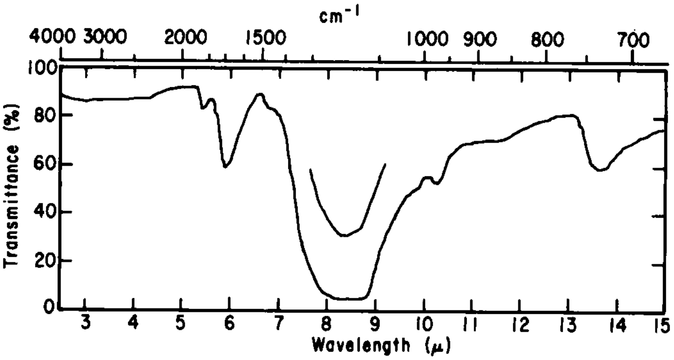

FIG. 6. Infrared spectrum of plasma polymerized tetrafluoroethylene film.

Figure 6 shows the IR spectrum of a polymer film deposited on a NaCl window placed in a TFE discharge. The strong broad absorption at 1100-1300 cm^{-1}, which is assigned to C—F vibrations, is identical with that observed in commercial polytetrafluoroethylene (PTFE). However, other relatively weak peaks do not match those found in PTFE. The carbonyl bond at 1700 cm^{-1} suggests oxidation of the film after exposure to air in a manner similar to that for other plasma-polymerized polymers. Notice, however, that a hydroxyl peak at 3400 cm^{-1} is not observed in Fig. 6.

While TFE and ethylene bear a close structural resemblance, their mechanisms of polymerization are expected to be quite different. The first evidence for this can be obtained by a comparison of the heats of reaction associated with Reactions (6) through (7b):

$$e + C_2F_4 \rightarrow C_2F_2 + F_2 + e, \quad \Delta H = 162.4 \text{ kcal/mole} \tag{6}$$

$$\rightarrow C_2F_2 + 2F\cdot + e, \quad \Delta H = 200.2 \text{ kcal/mole} \tag{6a}$$

$$\rightarrow 2CF_2\!: + e, \quad \Delta H = 70.4 \text{ kcal/mole} \tag{6b}$$

$$e + C_2H_4 \rightarrow C_2H_2 + H_2 + e, \quad \Delta H = 41.7 \text{ kcal/mole} \tag{7}$$

$$\rightarrow C_2H_2 + 2H\cdot + e, \quad \Delta H = 145.0 \text{ kcal/mole} \tag{7a}$$

$$\rightarrow 2CH_2\!: + e, \quad \Delta H = 171.7 \text{ kcal/mole} \tag{7b}$$

It is immediately obvious that the preferred dissociation products for TFE are expected to be difluoromethylene radicals. In contrast, the preferred dissociation products for ethylene are acetylene and molecular hydrogen.

Substantiation for the presence of the difluoromethylene radical has been obtained by Atkinson [14] and by Cohen and Heicklen [15] from studies of the mercury-sensitized photolysis of TFE. Both studies concluded that the formation of CF_2: was a primary process and that perfluorocyclopropane, formed by the reaction

$$CF_2: + C_2F_4 \rightarrow c\text{-}C_3F_6 \qquad (8)$$

was a major product. In Atkinson's study a polymeric product was also observed.

In a study of the direct photolysis of TFE, Dacey and Littler [16] have suggested that the perfluorocyclopropane formed in Reaction (8) is activated further to form additional radicals by the following sequence of steps:

$$c\text{-}C_3F_6 \rightarrow c\text{-}C_3F_6{}^* \qquad (9)$$

$$c\text{-}C_3F_6{}^* \rightarrow C_3F_6{}^* \qquad (10)$$

$$C_3F_6{}^* \rightarrow CF_3\cdot + CF_2{=}CF\cdot \qquad (11)$$

The $C_2F_3\cdot$ radical was believed to be responsible for the formation of higher molecular weight products at low pressures.

In the light of these observations it seems reasonable to conclude that the primary free radical derived from TFE is CF_2:. This is in direct contrast with ethylene where the primary radical is believed to be $H\cdot$.

Effects of Halogen-Containing Additives on the Plasma Polymerization of Hydrocarbons

As noted above, the presence of halogen atoms in the gas phase is expected to aid in the formation of the free radical precursors to polymerization through reactions such as (4) and (5). To explore this effect in further detail, various halogen-containing compounds were added during the polymerization of ethylene, ethane, and methane.

Figure 7 shows the dramatic effect on the rates of polymer deposition for ethylene and ethane when small amounts of dichlorodifluoromethane (Freon 12) are added to a constant monomer flow of 80 cm^3/min at STP. The polymer deposition rate for ethylene increases by more than a factor of 10 upon addition of 10% dichlorodifluoromethane, and under these conditions powder formation is rigorous. The film deposition rate for ethane, which is otherwise an order of magnitude smaller than that for ethylene, is increased to a

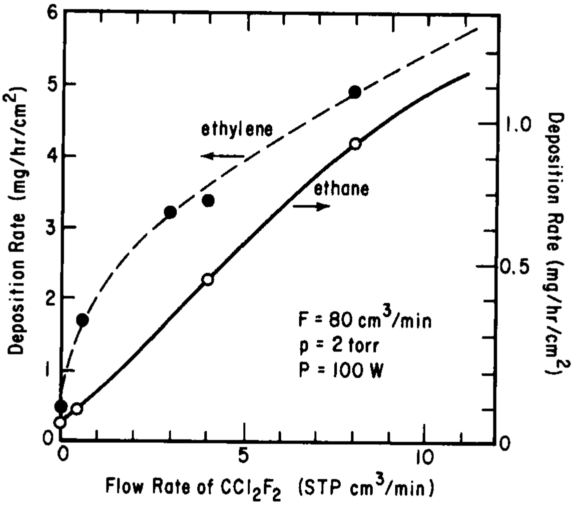

FIG. 7. The effect of CCl_2F_2 addition to ethylene and ethane on their polymer deposition rates.

level comparable to that for ethylene by addition of 5% dichlorodifluoromethane. When the additive flow rate is 20% of that of ethane, a powder is produced at a rate which is 30 times higher than the original polymerization rate.

The effects of adding CF_2Cl_2, CH_3Cl, and CF_4 on the polymerization of methane are illustrated in Fig. 8. In this instance it is noted that the addition of 10 cm^3/min of CF_2Cl_2 to a flow of 50 cm^3/min of methane increases the polymer deposition rate 50-fold over that for methane alone. The addition of CF_4 is observed to have a negligible effect, and CH_3Cl has an intermediate effect on the rate of polymer deposition.

As a test of the extent to which the halogenated additives polymerized by themselves, each was subjected to a discharge at 0.5 Torr and 100 W. The results shown in Fig. 9 indicate that only CH_3Cl polymerizes at an appreciable rate. These results suggest that CF_2Cl_2 and CF_4 behave as gas phase catalysts when added to methane. By contrast, CH_3Cl acts as both a catalyst and a monomer.

Representative compositions of the polymers formed when a halogenated compound is added to methane are shown in Table 1. The polymer composition obtained from methane and vinyl chloride separately are also shown. Two points are immediately obvious. The first is that the use of either CF_2Cl_2 or CH_3Cl causes a negligibly small amount of chlorine to be incorporated into the polymer. The second

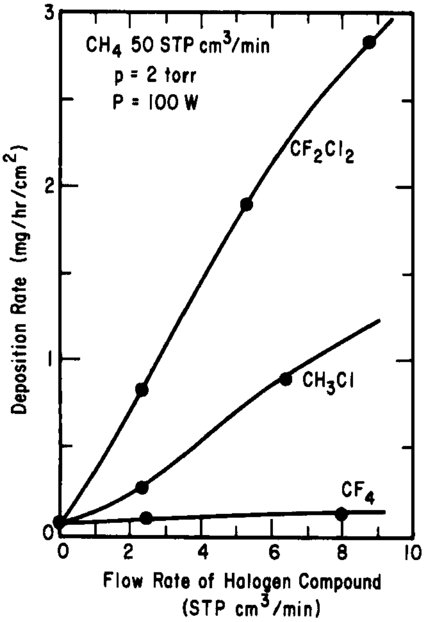

FIG. 8. The effects of addition of CF_2Cl_2, CH_3Cl, and CF_4 on the polymer deposition rate of methane.

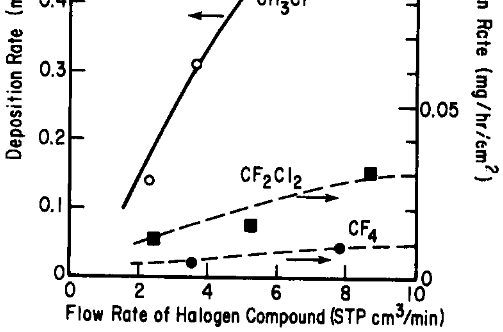

FIG. 9. The deposition rates of CF_2Cl_2, CH_3Cl, and CF_4.

TABLE 1. Compositions of Plasma Polymerized Polymer[a]

Monomer	(STP cm^3/min)		Empirical formula of polymer film
CH_4	(5.0)		$CH_{2.40}$
CH_4	(50)	Mixture	$CH_{1.62}Cl_{0.008}$
CF_2Cl_2	(2.3)		
CH_4	(50)	Mixture	$CH_{1.49}Cl_{0.02}$
CH_3Cl	(6.4)		
CH_3Cl	(6.4)		$CH_{0.80}Cl_{0.46}$

[a] Pressure, 2 Torrs; power, 100 W.

point is that the H/C ratio of the polymer prepared from a mixture of methane and CH_3Cl or CF_2Cl_2 is considerably smaller than that of a polymer prepared from methane alone.

In order to interpret the mechanism by which halogenated derivatives of methane can enhance the rate of methane polymerization, it is first necessary to examine the polymerization mechanism. We have proposed [3] previously that the initial step of this mechanism is the dissociation of methane by

$$e + CH_4 \rightarrow CH_2\!: + H_2 + e, \quad \Delta H = 105.9 \text{ kcal/mole} \tag{12}$$

$$\rightarrow CH_3\cdot + H\cdot + e, \quad \Delta H = 104 \text{ kcal/mole} \tag{12a}$$

The free radicals thus formed are then available to react further, yielding products of increasing molecular weight. Examples of these reaction step are

$$CH_2\!: + CH_4 \rightarrow C_2H_6{}^* \rightarrow C_2H_4 + H_2 \tag{13}$$

$$2CH_3\cdot + M + M \rightarrow C_2H_6 + M \tag{14}$$

$$CH_3\cdot + C_2H_4 + M \rightarrow CH_3CH_2CH_2\cdot + M \tag{15}$$

where M represents an unspecified molecule. The final polymer is formed through a complex combination of processes including free radical recombination and addition to unsaturated intermediates such as ethylene (see Reaction 13).

Because methane polymerizes very slowly by comparison to unsaturated hydrocarbons, it is believed that the formation of unsaturated derivative monomers (viz., ethylene or acetylene) is a slow step and that, consequently, the major path for polymerization is via radical recombination:

$$R_m\cdot + R_n\cdot \rightarrow R_{m+n} \tag{16}$$

Therefore the formation of new radicals of hydrocarbon molecules is the crucial reaction for the polymerization process. The two major pathways for this step are anticipated to be dissociation by electron collision and hydrogen atom abstraction:

$$RH + e \rightarrow R\cdot + H\cdot + e \tag{17}$$

$$RH + H\cdot \rightarrow R\cdot + H_2 \tag{18}$$

Typical activation energies for process such as Reaction (18) are 7.0 and 6.8 kcal/mole [17] if RH is methane or ethane, respectively.

When halogenated derivatives of methane are introduced into a discharge, it is expected that they will dissociate by processes such as

$$e + CF_2Cl_2 \rightarrow CF_2: + Cl_2, \quad \Delta H = 74.0 \text{ kcal/mole} \tag{19}$$

$$\rightarrow CF_2Cl\cdot + Cl\cdot, \quad \Delta H = 78.5 \text{ kcal/mole} \tag{19a}$$

$$e + CH_3Cl \rightarrow CH_2: + HCl, \quad \Delta H = 90.7 \text{ kcal/mole} \tag{20}$$

$$\rightarrow CH_3Cl\cdot + Cl\cdot, \quad \Delta H = 84.4 \text{ kcal/mole} \tag{20a}$$

$$e + CF_4 \rightarrow CF_2: + F_2, \quad \Delta H = 179.5 \text{ kcal/mole} \tag{21}$$

$$\rightarrow CF_3\cdot + F\cdot, \quad \Delta H = 119.5 \text{ kcal/mole} \tag{21a}$$

The ease with which such reactions will occur varies considerably depending on the structure of the compound, as suggested by the heats of reaction [18]. Comparison of Reactions (19) through (21a) with (12) and (12a) indicates that CF_2Cl_2 and CH_3Cl require considerably less energy to dissociate than CH_4. The opposite is true for CF_4. These observations lead us to expect that CF_2Cl_2 and CH_3Cl should act as copious free radical sources when added to methane because of their relative ease of dissociation, a conclusion which is consistent with the observations of Fig. 8. Correspondingly, CF_4 is expected to have very little effect on the rate of CH_4 polymerization.

In addition to forming free radicals by direct dissociation, CF_2Cl_2 and CH_3Cl release chlorine atoms which can abstract hydrogen from hydrocarbon intermediates and the growing polymer. This reaction can be represented by

$$RH + Cl\cdot \rightarrow R\cdot + HCl \tag{22}$$

Typical activation energies for a reaction such as Reaction (22) are 3.9 and 1.0 kcal/mole [19] if RH is taken to be methane or ethane, respectively. These values are considerably lower than for hydrogen abstraction via hydrogen atoms, Reaction (18). Consequently, the polymerization rate of methane should be enhanced by the presence of chlorine atoms.

Direct evidence for hydrogen abstraction by chlorine atoms can be found by examination of Table 1. It may be seen there that the H/C ratio in the polymer decreases consistently with an increasing Cl/H ratio in the mixture fed to the discharge.

Finally, the elementary reactions just discussed can be used to interpret the relative rates of polymer deposition shown in Fig. 9. The heats of reaction associated with Reactions (19) through (20a) indicate that CF_2Cl_2 should dissociate somewhat more easily than CH_3Cl. However, Fig. 9 shows that CH_3Cl polymerizes at a considerably faster rate than CF_2Cl_2. The explanation for this discrepancy is most likely due to the fact that reactions such as

$$Cl\cdot + CF_2Cl_2 \rightarrow CF_2Cl\cdot + Cl_2 \tag{23}$$

have a high activation energy. This is suggested by the known activation energy for chlorine atoms reacting with CCl_4 which is greater than 12 kcal/mole [20]. By contrast, the reaction

$$Cl\cdot + CH_3Cl \rightarrow CH_2Cl\cdot + HCl \tag{24}$$

is expected to have a much lower activation energy as suggested by the data associated with Reaction (22).

The extremely low polymer deposition rate for CF_4 is probably due to two factors. The first is its relatively high dissociation energy. The second is that the reaction

$$F\cdot + CF_4 \rightarrow CF_3\cdot + F_2 \tag{25}$$

which is similar to Reaction (23), is expected to have a high activation energy. Therefore both the original formation and the subsequent reformation of free radicals are slow processes.

ACKNOWLEDGMENT

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