FAST-FLOW MICROWAVE DISCHARGE STUDIES OF THE SYSTEM CARBON TETRAFLUORIDE–CARBON TETRACHLORIDE

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SUMMARY

Fast-flow microwave-induced glow discharge studies were carried out in systems containing CCl_4 and CF_4 at pressures in the region of 10–100 mTorr. The purpose of these investigations was to obtain information bearing on possible mechanistic steps in similar mixtures under γ-radiolysis. It was found that fragments from a discharge in CF_4 readily attack CCl_4 added downstream by displacement and abstraction processes giving chlorofluoromethanes and there is a similar although much less extensive attack of fragments from CCl_4 reacting with CF_4. Two-carbon fragments were noted in the mass spectrometer used to monitor the reactions only from discharges containing both compounds, indicating formation of chlorofluoroethanes by radical–radical combination reactions. There is some evidence for reactions involving difluorocarbene. These and other observations are consistent with the results of radiolysis experiments.

INTRODUCTION

Fast-flow microwave discharge experiments have been found to be a useful method for investigating reaction mechanisms and identifying reactive intermediates[1,2]. It occurred to us several years ago[3] that it would be fruitful to conduct parallel studies, under glow discharge conditions, of simple gas-phase systems which we were investigating from the viewpoint of radiation chemistry. The present series of experiments was prompted by the desire to understand the mechanism of the radiation chemistry of gas-phase mixtures of CCl_4 and CF_4[4]. Two types of experiments were done. In the downstream experiments, one reactant was decomposed by a microwave discharge and the other reactant was added downstream. Products formed by reaction of fragments produced in the discharge with the downstream additive were continuously monitored by a Bendix time-of-flight mass spectrometer. In the second type of experiment, CCl_4 and CF_4 were

first mixed then passed through the discharge. Product yields were studied as a function of mixture composition.

The fast-flow glow discharge decomposition of CCl_4 was previously studied in this laboratory[3], with ammonia gas added downstream. Heicklen[5] has studied the glow discharge reactions of CF_4 with ethylene added downstream. Other discharge experiments of both CF_4 and CCl_4 have been summarized by McTaggert[6].

EXPERIMENTAL

Apparatus

The apparatus used is shown in Figure 1. The reaction tube F was made of 11 mm Pyrex tubing and was 60 cm long. The downstream end was attached directly into the ion source of a Bendix model 14-107 time-of-flight mass spectrometer. A portion of the reaction mixture was sampled through a 400 μ orifice O
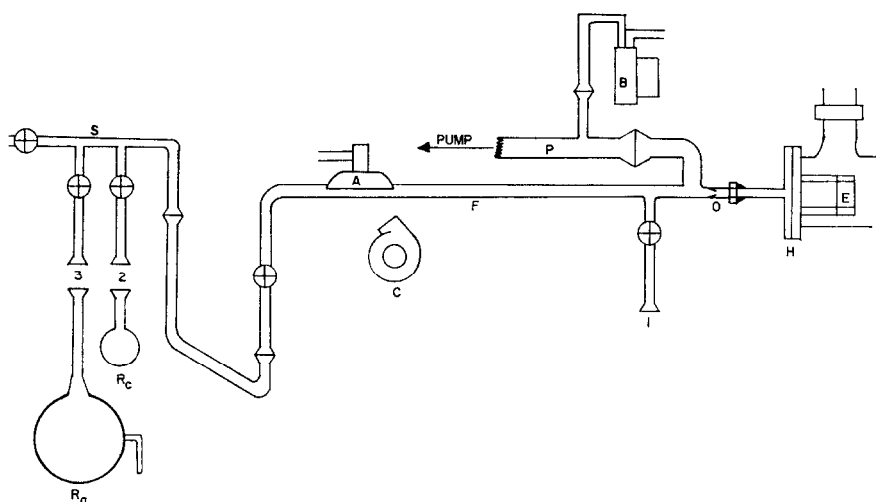

Fig. 1. Fast-flow microwave discharge system.

and the remainder was pumped away through the 17 mm pumping line P which attached to a 2 in oil diffusion pump. Sub-manifold S, which was part of a conventional glass vacuum system, was used for reactant preparation and storage. Reactants in R_a and R_c could be admitted through any of three inlets (1, 2 and 3), each of which was equipped with a Teflon needle valve. These were used to adjust the pressure in the flow tube F. The pressures were monitored by an M. K. S. Baratron capacitive micromanometer B. The microwave power was supplied by a 100 W Raytheon generator operating at 2450 MHz. The "type A" dish antenna A could be positioned from 0 to 50 cm from the sampling orifice O. The discharge zone was cooled by a stream of air from a squirrel cage blower C.

The flow rate at 30×10^{-3} Torr was found by loss of CCl_4 from R_c to be 5 m s^{-1}. An approximate correction was made for the different viscosity of CF_4. Assuming ideality, the flow rate for CF_4 at this pressure would be 6 m s^{-1}.

Reagents

Air Products 99.7% pure CF_4 was passed through a BaO drying tube into a storage bulb on a vacuum line and deaerated by four freeze–pump–thaw cycles. The purity of this CF_4 was checked on a flame ionization gas chromatograph and the only impurities found were $\simeq 10^{-4}$ mole% CF_3Cl and C_2F_6.

Mallincrodt analytical reagent grade CCl_4 was purified by degassing 2000 ml and irradiating it for 48 h. It was then distilled on a Todd still and the middle one-third collected. The only impurity found was about 10 ppm $CHCl_3$.

Product analysis

The abundance of each product was monitored mass spectrometrically by observing a carefully selected mass peak for each. Generally the ion chosen was the most intense one in the mass spectrum of that compound and also one that was produced only in low abundance by other compounds. Table 1 shows which ions were usually monitored. Under the experimental conditions used, masses 44, 54 and 70 could be assigned to CO_2, ClF and Cl_2, respectively. For other ions the situation was somewhat more ambiguous, due to the lack of detailed information on radical concentrations. Some radicals may be reaching the ion source; however, experiments by McDonald and Goll seem to indicate that the concentration of polyatomic radicals reaching the ion source would be small[7].

TABLE 1

IONS MONITORED IN MICROWAVE DISCHARGE EXPERIMENTS

m/e Monitored	Ion	Probable parent*
199	$C_2Cl_5^+$	C_2Cl_6, $(C_2Cl_5\bullet)$
164	$C_2Cl_4^+$	C_2Cl_4, C_2Cl_6
151	$CF_3CCl_2^+$	CF_3CCl_3, $(CF_3CCl_2\bullet)$
119	$C_2F_5^+$	C_2F_6, $(C_2F_5\bullet)$
117	CCl_3^+	CCl_4, $(CCl_3\bullet)$
101	$CFCl_2^+$	$CFCl_3$, $(CFCl_2\bullet)$
100	$C_2F_4^+$	C_2F_4
85, 86, 87	SiF_3^+	SiF_4, $(SiF_3\bullet)$
85, 86	CF_2Cl^+	CF_3Cl, CF_2Cl_2, $(CF_2Cl\bullet)$
70	Cl_2^+	Cl_2
69	CF_3^+	CF_4, $(CF_3\bullet)$
54	ClF^+	ClF
44	CO_2^+	CO_2

* Contribution from species in parentheses is not known.

It appears that only neutral species are diffusing into the ion source. In a brief series of experiments, the electron beam in the mass spectrometer was turned off while the discharge was on and the machine was put into various modes of operation. No ions were seen. This is in agreement with the generally held opinion that the chemically active species downstream from a discharge are neutral[8]. Ions persist but in concentrations too low to account for the amount of chemical reaction seen.

RESULTS AND DISCUSSION

CCl₄ downstream

In these experiments CF_4 at 20 μ was passed through the discharge while CCl_4 at 5 μ was bled in downstream through inlet 1. The position of antenna A was varied from 7.5 to 35 cm from the downstream inlet. Since the flow velocity was 6 m s⁻¹, the time required to traverse the distance between the edge of the discharge and the downstream inlet could be estimated to vary from 4 to 50 ms. The results of these experiments are shown in Figure 2 where it can be seen that the CCl_4 is being attacked by fragments from the CF_4 discharge even from the distance of maximum separation (35 cm).
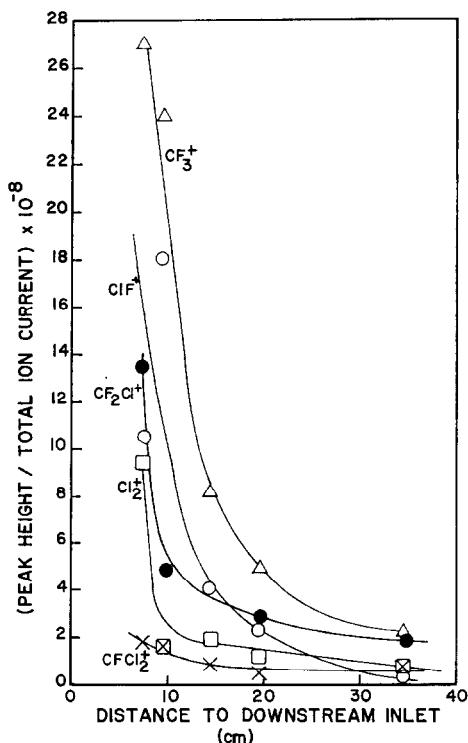

Fig. 2. Effect of distance between CF_4 discharge and CCl_4 added downstream.

A "blank" run was made in which CF_4 (20 μ) was passed through the discharge but no CCl_4 was added downstream. As in the preceding experiment, the position of the antenna was varied and the ion intensities were monitored. The results of these experiments are shown in Figure 3 and clearly demonstrate reaction with the walls of the flow tube with the resultant formation of SiF_4. As shown in Table 1, SiF_3^+ comes from ionization of SiF_4 and possibly some SiF_3 radicals. As the distance to the mass spectrometer inlet was decreased, a decrease in the amount of SiF_3^+ was observed along with a corresponding increase in the amount of CF_3^+. These changes are similar to those seen when CCl_4 was added downstream.
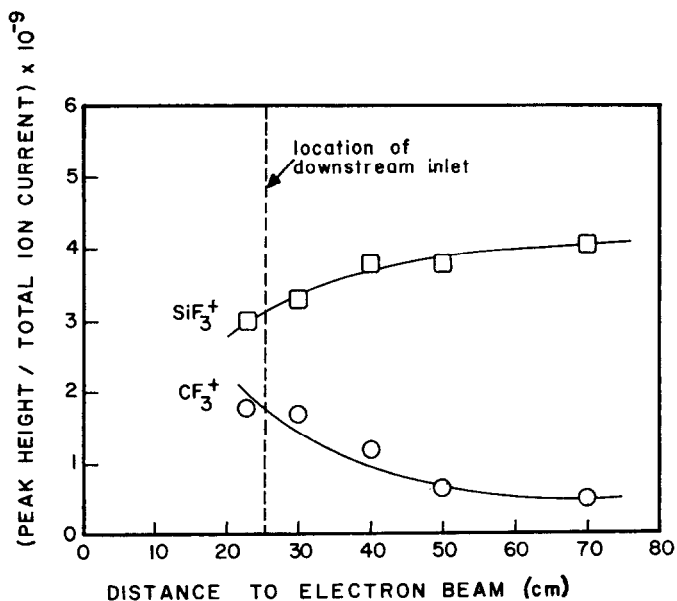

Fig. 3. Effect of distance to ion source on SiF_3^+ from CF_4 discharge.

It was hoped that these experiments would aid in formulating a mechanism for the radiolysis, particularly for the mechanism of formation of CF_2Cl_2. It was thought that CF_2Cl_2 was formed by reaction of CF_2 and CCl_4, but no proof of this reaction could be devised[4]. It is possible to obtain information about CF_2Cl_2 formation from the present results, but a complex process of curve subtraction must be followed. The reason is that CF_2Cl_2 does not give its parent ion under electron bombardment. The ion CF_2Cl^+ does occur, but unfortunately this ion also arises from CF_3Cl which is present in this system.

In order to estimate how much of the CF_2Cl^+ peak in Figure 2 is due to CF_2Cl_2, it is necessary to subtract the portion due to CF_3Cl. First the amount of CF_3Cl present is inferred from the CF_3^+ peak at mass 69; then the corresponding yield of CF_2Cl^+ arising from CF_3Cl (as judged from its mass spectral cracking

pattern[9]) is subtracted from the mass 85 peak. However, as seen in Figure 3, a "background" amount of CF_3^+ ion arising from the CF_4 (which has passed through the discharge) is also present.

If the "background" CF_3^+ curve (Fig. 3) is subtracted from the CF_3^+ curve in Figure 2, the resultant CF_3^+ intensity is that due to CF_3Cl. In subtracting the two CF_3^+ curves the "background" curve (Fig. 3) had to be shifted down slightly to coincide with the CF_3^+ curve in Figure 2 at the 35 cm point. This is justified by the experimental observation that the intensity of CF_3^+ is not affected by the addition of small amounts of CCl_4 at long distances downstream. The ratio of mass 85 (CF_2Cl^+) to mass 69 (CF_3^+) in the mass spectrum of CF_3Cl is 0.3[9]. Thus, one-third of the "net CF_3^+" curve can be taken to be the contribution of CF_3Cl to the CF_2Cl^+ curve in Figure 2. If this is subtracted from the CF_2Cl^+ curve in Figure 2 the remainder is the contribution due to CF_2Cl_2. The resolution of the CF_2Cl^+ curve into its two components is shown in Figure 4.
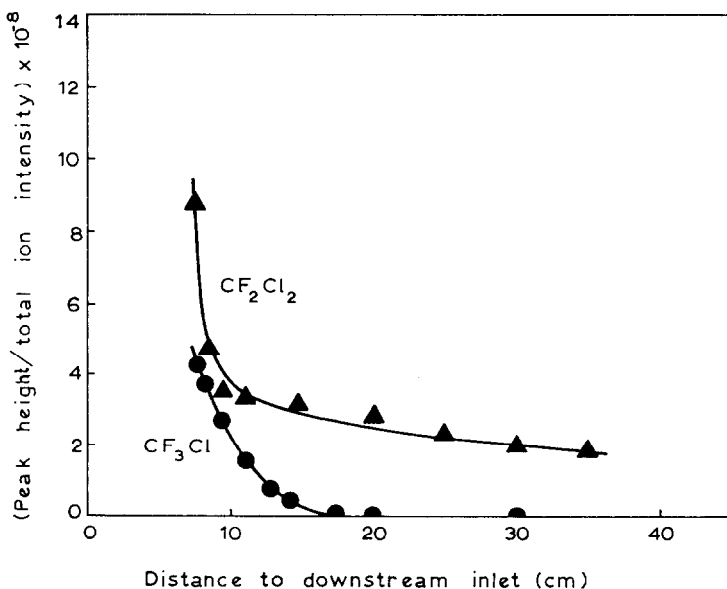

Fig. 4. Production of CF_3Cl and CF_2Cl_2 from CCl_4 added downstream from CF_4 discharge.

Although curve subtraction introduces increased error, it appears that both CF_3Cl and CF_2Cl_2 are formed when CCl_4 is added downstream. Furthermore, CF_3Cl is formed from a much more short-lived species than CF_2Cl_2. This behavior is exactly what would be expected if, as postulated in the radiolysis mechanism, CF_3Cl is being formed by CF_3 radical attack on CCl_4 and CF_2Cl_2 is being formed by CF_2 radical attack on CCl_4. From studies of emission bands[10] and absorption bands[11], it appears the CF_2 radicals from an electrodeless discharge in CF_4 are

produced in the singlet state. From observations of the chemical reactivity of CF_2 from a glow discharge in CF_4, however, it seems that the triplet state is present[5]. From the CF_2Cl_2 production curve in Figure 4, it appears that both singlet and triplet CF_2 may be present and reacting with CCl_4 to give CF_2Cl_2. The triplet state is more reactive and is assumed to be responsible for the steep portion of the CF_2Cl_2 production curve[5].

Also of considerable interest in this experiment was the production of ClF. Although it was not shown to be present in the radiolysis system, it was considered as a possible reactive intermediate. Reactions (1) and (2) show its postulated role:

$$F• + CCl_4 \rightarrow CCl_3• + ClF \qquad (1)$$

$$ClF + CCl_4 \rightarrow CFCl_3 + Cl_2 \qquad (2)$$

Reaction (1) is slightly endothermic ($\Delta E = +7\pm3$ kcal mole^{-1})[12] while reaction (2) is exothermic by 30 kcal mole^{-1}. Another energetically favorable reaction forming ClF ($\Delta E = -66$ kcal mole^{-1}) would be reaction (3):

$$F_2 + CCl_4 \rightarrow CFCl_3 + ClF \qquad (3)$$

Carbene insertion reactions such as reaction (4) are very favorable energetically ($\Delta E \simeq -69$ kcal mole^{-1}), but no evidence for the production of this dimer was found:

$$CF_2 + CCl_4 \rightarrow CF_2ClCCl_3* \qquad (4)$$

It is possible that this reaction has a high activation energy or that the excited dimer thus produced decomposes rapidly (lifetime less than about 20 ms).

CF$_4$ downstream

These experiments were analogous to those in the preceding section, but now CCl_4 at 20 μ was decomposed in the discharge and the fragments were allowed to react with CF_4 which was added downstream at 5 μ. The results are shown in Figure 5. The very large amount of Cl_2 was formed whether or not CF_4 was added downstream. When the discharge was turned on with only CCl_4 in the flow tube the intensity of CCl_3^+ (from CCl_4) decreased by about 90%. This is indicative of the great extent of decomposition in the discharge. Brown polymeric material built up rapidly on the walls of the tube in the discharge zone. Because of the high carbon–fluorine bond dissociation energy (121 kcal mole^{-1}) in CF_4 it is normally considered to be very non-reactive. Figure 5, however, shows that in this system $CFCl_3$ and some CF_2Cl_2 and/or CF_3Cl are formed. Additional evidence for the decomposition of CF_4 was supplied from the small yield of SiF_4 seen when the antenna was closest to the downstream inlet. Few reactions with CF_4 are energetically favorable. One favorable class of reactions is carbene insertion such as reaction (5):

$$CCl_2 + CF_4 \rightarrow CFCl_2CF_3 \qquad (5)$$

While the reaction is exothermic by about 69 kcal mole^{-1}, no evidence for this reaction was seen in these experiments.
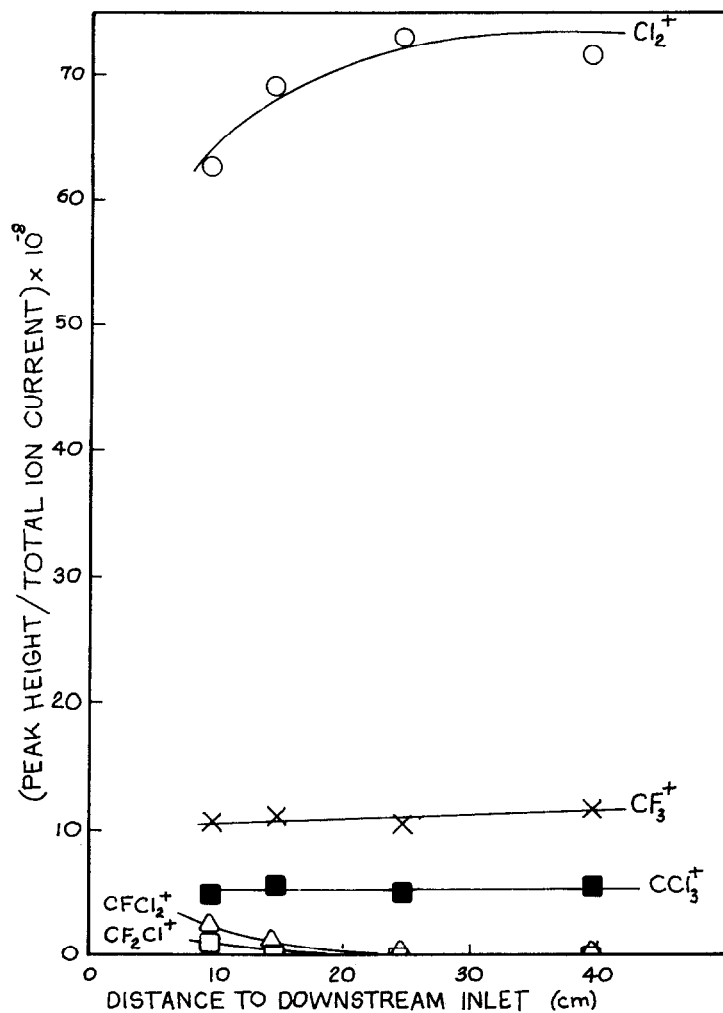

Fig. 5. Effect of distance between CCl_4 discharge and CF_4 added downstream.

Also of interest is the lack of ClF formation. Evidently reaction (6), which is endothermic by 35 kcal mole^{-1}, does not occur.

$$Cl_2^* + CF_4 \rightarrow CF_3Cl + ClF \tag{6}$$

Also ruled out by the absence of ClF would be the abstraction of F atom from CF_4 by Cl atoms.

Lastly, the yield of $CFCl_3$ (inferred from the ion $CFCl_2^+$) suggests a new source of this product in the radiolysis experiments. Reaction (7) is endothermic[12] by 19 ± 11 kcal mole^{-1}, but it may proceed by reaction of an excited CCl_3 radical.

$$\cdot CCl_3^* + CF_4 \rightarrow CFCl_3 + CF_3 \cdot \tag{7}$$

Translationally and electronically excited species commonly arise in radiation chemistry as the result of ion formation and charge neutralization reactions.

Mixed discharge as a function of composition

Mixtures ranging from 16 to 58 mole% CCl_4 were studied with the antenna placed 30 cm from the sampling orifice. The flow tube[3] used in these experiments was functionally similar to that shown in Figure 1. It differed in that the sampling orifice was a 40 μ hole in a gold foil placed about 5 mm from the ion source. The pumping lines on this apparatus were more constricted and thus the time to traverse the distance from the edge of the discharge to the ion source was about 170 ms. The pressure of CCl_4 was maintained at 28 μ while the pressure of CF_4 was varied from 17 to 152 μ. Ion intensities were measured in centimeters from the mass spectrum recorded on an oscillograph. The results of these experiments are shown in Figures 6 and 7 where the ion intensity is plotted against the mole% CCl_4 in the reactant mixture.

At the maximum CCl_4 concentration the main product was Cl_2 along with small and nearly equal amounts of C_2Cl_4 and C_2Cl_6. Similar relative amounts of Cl_2, C_2Cl_4 and C_2Cl_6 were formed when pure CCl_4 was passed through the discharge. Brown polymeric material built up rapidly on the walls of the reaction tube as in the case of the pure CCl_4 discharge. When only CF_4 was present in the discharge a white deposit was formed on the walls of the tube. As the concentration of CCl_4 is decreased, $C_2Cl_5^+$ and $C_2Cl_4^+$ gradually decrease while $C_2F_4^+$, $C_2F_5^+$, SiF_3^+ and CF_2Cl^+ rapidly increase in a nearly linear manner. In contrast, $C_2F_3Cl_2^+$, $C_2F_4Cl^+$ and $CFCl_2^+$ each go through a maximum around 30 mole% CCl_4. There is some curvature in plots for $C_2F_4^+$ and $C_2F_5^+$ indicating that they may also be going through maxima as indicated by the dotted line. This is substantiated by experiments such as shown in Figure 3 where only CF_4 was present in the discharge and no $C_2F_4^+$ or $C_2F_5^+$ were observed to be produced.

In both the radiolysis and the microwave discharge the C_2Cl_6 yield is approximately equal to the C_2Cl_4 yield and both yields are much smaller than the yields of other products. The remaining dimer yields are much greater in the microwave discharge experiments, notably C_2F_4 which is not found at all in the radiolysis. Tetrafluoroethylene is thought to be a reactive intermediate in the radiolysis system, going on to form polymer. Proof that it can be formed in CCl_4–CF_4 mixtures was obtained from these mixed microwave discharge experiments (Fig. 7) where more of it was formed as more CF_4 was added to the mixture. This behavior is similar to that shown by the polymer formation in the radiolysis experiments.

Dimer products containing both chlorine and fluorine go through maxima (Figs. 6 and 7) when large amounts of both reactants are present in the mixed discharge. This would seem to indicate that these products arise from the combination of free radicals produced from both reactants. This is substantiated by the fact that dimer products were not seen in the downstream experiments.
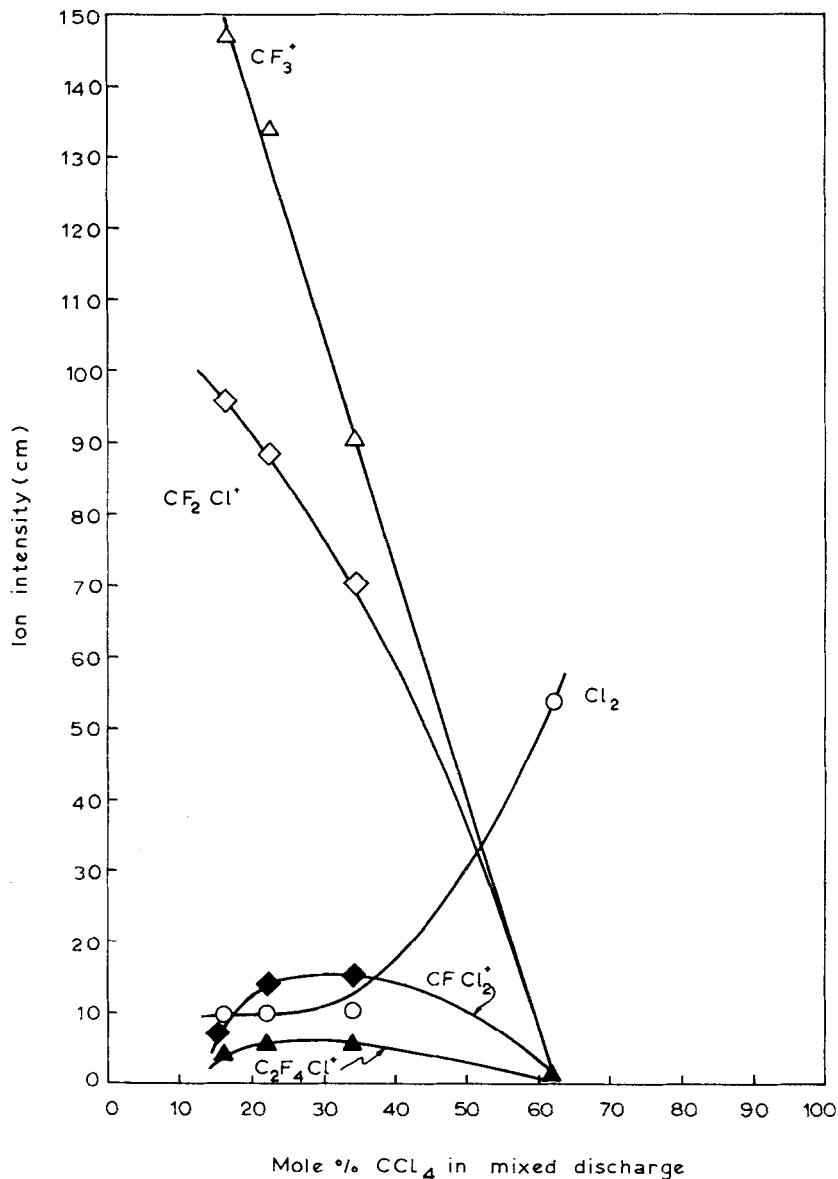

Fig. 6. Effect of composition in mixed CCl_4–CF_4 discharge.
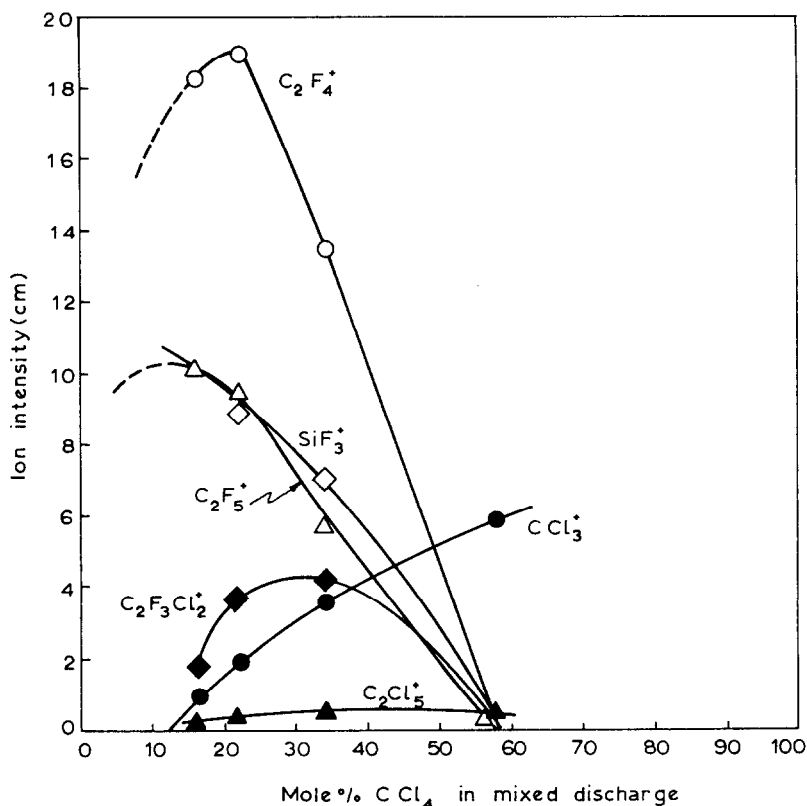
Fig. 7. Effect of composition in mixed CCl_4–CF_4 discharge.

Unlike the radiolysis, the Cl_2 yield is very large compared to other products from the discharge mixtures containing mostly CCl_4. It was also very much larger than CCl_3^+ (from CCl_4) which indicates the very extensive amount of decomposition taking place in the discharge. Large amounts of Cl_2 formation were accompanied by large amounts of polymer formation. In the radiolysis the amount of decomposition seldom exceeded 1%, while in the discharge it appeared to approach 90%. The two methods might become more comparable if the radiolysis were carried out at very high dose rates and low pressures. In the present experiments the rate of energy input in the microwave discharge experiments was about 10^8 times greater than in the radiolysis experiments and the pressure was 10^4 times lower than in the radiolysis.

It is felt that fast-flow microwave discharge experiments show considerable promise as a tool for the elucidation of the mechanism of radiolysis reactions. In the present studies, however, we found that attack of fluorine-containing fragments on the Pyrex flow tube walls led to formation of SiF_4 which complicated the results. In subsequent work we have turned to a nickel flow system to alleviate this difficulty.

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