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RADIATION SYNTHESIS INVOLVING HALOGEN COMPOUNDS

Final Report: May 1, 1960, through October 31, 1965

By
Paul Y. Feng

May 5, 1966

IIT Research Institute
Chicago, Illinois

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RADIATION SYNTHESIS INVOLVING HALOGEN COMPOUNDS

Final Report, May 1, 1960, through October 31, 1965

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IITRI Project U6026

Prepared by

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May 5, 1966

for

Division of Isotopes Development
United States Atomic Energy Commission
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FOREWORD

This is Report No. COO-578-3-32 (Final Report) on IITRI Project U6026, "Radiation Synthesis Involving Halogen Compounds," under Contract No. AT(11-1)-578, Project Agreement No. 3. This report covers the period from May 1, 1960, through October 31, 1965.

Personnel who contributed to this project included W. Bahmet, L. Bernstein, P. Feng, W. Glasson, K. Schmude, F. Vetovec, and J. Wurmel.

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Respectfully submitted,

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ABSTRACT

RADIATION SYNTHESIS INVOLVING HALOGEN COMPOUNDS

The objective of this program was the development of methods for synthesizing fluorine compounds by means of radiation-induced reactions. The feasibility of this method was established early in the project; thus most of the work was directed toward a better understanding of the radiation chemistry of selected fluorocarbons and the mechanism and reaction kinetics of the radiation-induced fluorination process.

Studies on the radiation chemistry of fluorocarbons were carried out either by using only a selected fluorocarbon as the irradiated material or by using the fluorocarbon mixed with other compounds that could react with the intermediate product by radiation. The radiation chemistry of CF_3Cl , CF_3Br , and CF_4 has been studied. The results show that despite the well-established thermal and chemical stability of the C-F bond, the radiation stability of the fluorocarbons is comparable with, though somewhat higher than, that of the hydrocarbons. Both ionic and radical intermediates are produced, and the primary G values are of the order of 2 to 3 or less. In addition, the C-F bond was found to be subject to attack by ionic intermediates, such as CF_3^+ , leading to the formation of the fluorine abstraction product, CF_4 .

Irradiation of mixtures of the simple fluorocarbons with aromatic hydrocarbons led to the formation of aromatic fluorine compounds with $G \sim 2$ to 3. Both radical and ionic processes contribute to the observed reaction process. The temperature effects for these processes, however, differ and thus afford a means of controlling the course of the radiation-induced fluorination reaction.

The existence of a relatively temperature-independent ionic mechanism and intermediates such as CF_2Cl^+ , CF_2Br^+ , CF_2I^+ , etc. suggest that the radiation method could be used in the preparation of heat-sensitive fluorine compounds, particularly those which may be expected to be valuable in biological and physiological applications.

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RADIATION SYNTHESIS INVOLVING HALOGEN COMPOUNDS

1. INTRODUCTION

The objective of this program was the development of methods for synthesizing fluorine compounds by means of radiation-induced reactions. The feasibility of this method was established early in the project; thus most of the work was directed toward a better understanding of the radiation chemistry of tetrafluoromethane, bromotrifluoromethane, and chlorotrifluoromethane and of the mechanism and reaction kinetics of the radiation fluorination process.

Studies on the radiation chemistry of fluorocarbons were carried out either by using only a selected fluorocarbon as the irradiated material or by using the fluorocarbon mixed with other compounds that could react with the intermediate produced by radiation. Particular emphasis was given to the radiation chemistry of chlorotrifluoromethane and carbon tetrafluoride. The former was selected as a promising reagent for the synthesis of fluorinated products capable of undergoing subsequent reactions, and the latter as a compound with proven ability to replace hydrogen by fluorine in aromatic compounds.

More specifically, the principal subject areas covered specific studies on the mechanisms and process variable kinetics peculiar to the radiation-induced fluorination reaction and the direct synthesis of fluorinated compounds with an aromatic structure.

2. BACKGROUND INFORMATION

Although the syntheses of the various chloro, bromo, and iodo compounds have been well developed and represent some of the best known organic chemical reactions, the application of these classical methods to the synthesis of organic fluorine compounds has often met with limited success. The considerable reactivity and corrosive properties of F_2 and hydrogen fluoride render the practical experimental aspects more difficult, but more important, many well-developed methods for the syntheses of organic halogen compounds are not useful in the syntheses of fluorinated products. For example, the direct interaction of Cl_2 or Br_2 with aromatic hydrocarbons can indeed lead to the formation of halogenated aromatic compounds under proper conditions. On the other hand, the interaction of F_2 with an aromatic hydrocarbon would only lead to a variety of degradation products such as CF_4 , among others. Similarly, a standard technique for the preparation of the alkyl halides is the interaction of an alcohol with the appropriate hydrogen halide. Nevertheless, alkyl fluorides cannot be obtained from the reaction of an alcohol with concentrated or even anhydrous hydrofluoric acid.

As a result, indirect methods have often been needed in the syntheses of organic fluorine compounds. Some of these methods, especially those involving aromatic compounds, may require several reaction steps and are therefore rather inconvenient or even impractical for the syntheses of compounds with more complicated or delicate structures.

In contrast with the classical methods, the radiation synthesis method requires only that a mixture of the compound to be fluorinated and a readily available noncorrosive fluorocarbon, such as CF_4 or CF_3Cl , be irradiated. The principle of the process, as indicated below, is simple.

etc.

In other words, a variety of reaction products reflecting the introduction of either the fluorine atom or substituents such as CF_3 or CF_2Cl can be formed in such a process and can be separated by such methods as gas or liquid chromatography. Furthermore, as the result of research on the mechanisms and process variables, the efficiency of the process can be predicted, and reasonable modification of the relative yields of the products can also be expected through controls of the conditions of irradiation.

3. RADIATION CHEMISTRY STUDIES

3.1. Fluorine Compounds

Relatively little information was available concerning the radiation chemistry of fluorine-containing compounds. The following review essentially covers the literature on this

subject up to the summer of 1965. Of particular significance is the observation by most researchers that, despite the well-established thermal stability of the carbon-fluorine bond, the radiation stability of the fluorine bond and the radiation stability of fluorine compounds are comparable to those of other organic compounds. It is this radiation sensitivity that makes possible the radiation synthesis process.

Among the earlier reports were those on studies on the effects of radiation on Teflon. Ryan (ref. 1) irradiated Teflon by cobalt 60 gamma rays and observed the formation of F_2 with $G(F_2) = 0.2$ to 0.5 . Charlesby (ref. 2), using radiation from a reactor, did not detect the formation of fluorine but instead observed C-C bond scission and the formation of CF_4 . Apparently, reactive species are produced when Teflon is irradiated, since Wall and Florin (ref. 3) observed significant differences in the extent of radiation-induced degradation between experiments conducted in vacuo and those conducted in the presence of oxygen.

The number of studies carried out on the radiation chemistry of fluorocarbons were limited. Feng and Mamula (ref. 4) irradiated mixtures of fluorocarbons such as CF_4 and C_6H_6 and its derivatives and concluded that fluorine-containing intermediates are produced by radiation with G values on the order of 2, and that ionic mechanisms play important roles in the radiation chemistry of fluorine compounds.

The ease of scission of the C-F bond was also observed by Silverman and co-workers (ref. 5), who irradiated CCl_3F in the liquid state with electrons. They found that the values of $G(\text{F})$ and $G(\text{Cl})$ were 0.16 and 0.62, respectively, i.e., almost in the F:Cl ratio. These results agree proportionately with those of Davidge (ref. 6) who irradiated CF_4 at 70°C in a reactor and found a $G(\text{F})$ of 0.56. Simon and Taylor (ref. 7) examined the effect of reactor irradiation on perfluoro-tributylamine, a mixture of the cyclic oxides perfluoro-(2-butyltetrahydrofuran) and perfluoro-(2-propyltetrahydropyran), and perfluoroheptane, and concluded that the G values for the disappearance of the original compounds are on the order of 2 to 3, as based on the amounts of the higher- and lower-boiling fractions formed after irradiation.

Similar results also were obtained when Heine (ref. 8) gamma-irradiated the same perfluoroamine, the cyclic oxide mixture, and perfluorooctane. Florin, Brown, and Wall (ref. 9) studied the gamma radiolysis of F_6H_6 and concluded that its radiation behavior is similar to that of the hydrogen compound.

More recently, Kevan and co-workers (ref. 10) studied the radiolysis of several simple fluorocarbons and again found G values on the order of 1 to 2 for a number of the products. They also found that nonradical mechanisms are involved in fluorocarbon radiolysis. Fallgatter and Hanrahan (ref. 11) studied the radiolysis of perfluorocyclohexane. These authors determined that the G values of the dimeric products were 2.2

for perfluorobicyclohexyl and 0.66 for perfluorocyclohexyl. Qualitatively, the radiation chemistry of perfluorocyclobutane was also studied, and the formation of dimeric and other high-molecular-weight products was again observed. Radiolysis of cyclic fluorocarbons was also studied by McKenzie, Bloch, and Wiswall (ref. 12) who found the G values for the destruction of the original material were 1.3 to 2.4.

3.2. Bromotrifluoromethane

A study of the radiation chemistry of CF_3Br was of interest in the program for at least two reasons. From the viewpoint of radiation synthesis, the weaker C-Br bond renders CF_3Br an interesting starting material for enhanced introduction of the CF_3 group. From the viewpoint of clarifying the mechanism of the fluorination reaction and thus better understanding and controlling the radiation chemical process, the large differences between the chemical properties of Br_2 and F_2 suggest that CF_3Br is a convenient and logical material in the study of radiation chemistry of the fluorocarbon system.

3.2.1. Experimental

3.2.1.1. Materials and Sample Preparation

The CF_3Br used in our experiments was obtained commercially and purified by bulb-to-bulb distillation under vacuum. The purified product so obtained was considered sufficiently pure for our experiments when only one peak was observed in the gas chromatograms obtained under conditions similar to those used for analysis of the irradiated samples. ACS-grade Br_2 was used without further purification.

The irradiation vessels were provided with breakseals, prebaked prior to attachment to the vacuum manifold, and further heated under vacuum. The irradiated samples were introduced to the vessels by using conventional vacuum-handling techniques and were sealed off under vacuum at liquid nitrogen temperature.

3.2.1.2. Irradiation and Analysis

Irradiations were carried out in the IITRI hot-cell facility by using either one or two cobalt 60 sources, which have nominal strengths of 1 kilocurie each. Temperature control was afforded by a conventional thermostated system. Radiation intensities were monitored routinely by means of ferrous sulfate dosimetry, which had been checked against the acetylene dosimetry system. Analyses were carried out gas chromatographically. A silica gel column was used for the CF_3Br and $\text{CF}_3\text{Br} + \text{Br}_2$ samples after the removal of the free Br_2 , which was either originally present in the samples or formed as a product of radiolysis. Temperature programming was used in these analyses since it considerably improved the sharpness of the peaks of the products.

3.2.2. Results

3.2.2.1. Effects of Total Dose

The experiments on the effects of total dose on the radiolysis of CF_3Br were carried out at 27°C (ambient temperature). The results of these experiments are given in Table 1. Apparently, within the limits of experimental accuracy, there is no appreciable variation in the $G(\text{CF}_4)$ and $G(\text{CF}_2\text{Br}_2)$ values over total dose, which ranged from 1.4×10^{21} to 6.1×10^{21} ev/gram.

Table 1
EFFECT OF TOTAL DOSE ON THE RADIOLYSIS
OF CF_3Br AT 27°C

Radiation Dose, 10^{20} eV/gram	Average G Values	
	CF_4	CF_2Br_2
1.42	1.51	1.25
6.71	1.45	1.41
12.65	1.44	1.41
17.75	1.47	1.58
30.87	1.53	1.44
43.71	1.50	1.78
61.81	1.45	1.72

3.2.2.2. Effects of Temperature

The effects of temperature on the radiolysis of CF_3Br were studied over the temperature range of 27 (ambient) to 300°C at a total radiation dose of approximately 1.74×10^{21} eV/gram. The results of these studies are given in Table 2 and show that increases in the temperature of irradiation lead to distinct increases in the CF_2Br_2 yield and to a small enhancement of the CF_4 yield. In addition, the yields of C_2F_6 and of another product, provisionally identified as C_2F_4 , also increased sharply with temperature, thereby accounting for the disparity between the CF_4 and CF_2Br_2 yields at the higher temperatures and providing an approximate material balance.

Table 2

EFFECT OF TEMPERATURE ON THE RADIOLYSIS OF CF_3Br

Temp., °C	Radiation Dose, 10^{20} eV/gram	Average G Values	
		CF_4	CF_2Br_2
27	17.8	1.47	1.58
125 $\pm$ 5	17.3	1.64	2.24
160	17.2	1.63	1.67
200	17.2	1.82	2.34
255 $\pm$ 5	17.3	1.83	2.27
300	17.4	1.84	3.15

3.2.2.3. Effect of Added Bromine

Comparison of the radiolytic results of CF_3Br with those of $\text{CF}_3\text{Br} + \text{Br}_2$ in Table 3 shows that bromine appears to enhance the yield of CF_2Br_2 . The yield of CF_4 is, however, not affected by the addition of bromine.

Table 3

COMPARISON OF RADIOLYSIS EXPERIMENTS
ON CF_3Br AND ON $\text{CF}_3\text{Br} + \text{Br}_2$

Radiation Dose, 10^{20} eV/gram	Br_2	Average G Values	
		CF_4	CF_2Br_2
2.04	No	1.5	1.5
	Yes	1.5	2.0
13.4	No	1.5	1.7
	Yes	1.4	2.0

3.2.3. Process Mechanism Considerations

3.2.3.1. CF₃Br Formation

Examination of the experimental data suggests that both ionic and radical intermediates are involved in the radiolysis of CF₃Br. The formation of CF₄, however, must be due to a mechanism involving only the ionic intermediate CF₃⁺. In general, fluorocarbons are considered to be inert toward attack by free radicals. However, considerable experimental evidence shows that the interaction of CF₃· radicals with perfluorinated compounds will not lead to the formation of the CF₄ molecule. Thus, for example, Ayscough and Steacie (ref. 13) observed that the photolysis of hexafluoroacetone produced C₂F₆ and CO in good yield, but no CF₄. This finding was later confirmed by Gordon (ref. 14). Similarly, Pritchard, Pritchard, Schiff, and Trotman-Dickenson (ref. 15) used hexafluoroazomethane as the source of CF₃· radicals. They did not observe CF₄ formation but instead observed the production of the recombination product, C₂F₆, as well as the addition of the radicals to the N:N bond. Such results, coupled with the experimental observation that the addition of Br₂ has no significant effect on CF₄ yield, necessarily lead to the conclusion that an ion-molecule process must be responsible for the observed formation of CF₄.

Our experimental results also showed that a small but definite temperature effect and consequently a positive energy of activation could be ascribed to the formation of CF₄ from the

radiolysis of CF_3Br . This observation, we believe, is not inconsistent with the postulation of an ion-molecule process, despite the fact that such processes are normally known to proceed with no observable energy of activation of temperature effect.

In principle, at least three alternate processes are possible when a CF_3^+ ion interacts with a CF_3Br molecule:

Although all these reactions should require little or no activation energy, as might be expected for ion-molecule processes, the efficiencies of these processes may nevertheless differ sufficiently from each other. In particular, the formation of CF_4 according to Reaction 2 requires the stretching and scission of a C-F bond along the reaction path and thus can be expected to require a positive energy of activation and to be relatively favored by increases in the reaction temperature. This was indeed observed in our experiments; the $G(\text{CF}_4)$ exhibited a small but definite increase as the temperature was increased from 27 to 300°C.

The foregoing consideration suggests that the abstraction of a fluorine atom from a CF_3Br molecule by the CF_3^+ ion may

proceed through (1) the polarization of a CF_3Br molecule by the electric field of CF_3^+ to become

and (2) the formation of a partial bond between the CF_3^+ ion and the polarized CF_3Br molecule accompanied by the simultaneous stretching and eventual breaking of the $\text{F}-\text{CF}_2\text{Br}$ bond.

On the basis of this mechanism, energy must be supplied to the system during the earlier phases of the fluorine abstraction process up to the point where the energy released by the formation of the CF_3^+-F bond is equal to the energy required to stretch the bond. In other words, an activation energy whose magnitude would depend, among other factors, on the ease of stretching the specific bond involved in the reaction would be required for the fluorine abstraction process. Consequently, in view of the great strength of the $\text{C}-\text{F}$ bond, it would be reasonable to assume that the energy of activation involved in the ion-molecule fluorine abstraction process is somewhat higher than those in other ion-molecule processes. (On the basis of similar considerations, the activation energy for the abstracting of fluorine atoms by radicals should also be higher than those for other radical abstraction processes; consequently, the $\text{C}-\text{F}$ bond is unable to undergo the radical abstraction reaction.)

By assuming that the yield of the CF_3^+ ions is independent of temperature, an Arrhenius plot of the G value of CF_4 versus

temperature would then provide an indication of the activation energy of the ion-molecule fluorine abstraction process. As shown in Figure 1, this plot gives an activation energy of about 0.39 kcal/mole, which is a rather small value, as can be expected for an ion-molecule reaction, and which would normally be obscured by other processes with higher energies of activation.

An ionic mechanism for CF_4 formation also agrees reasonably well with mass spectra data. On the basis of the W values of related fluorocarbons (ref. 16), the total yield of ions/100 eV during the irradiation of CF_3Br can be estimated to be on the order of 3 to 3.2. By assuming that, in analogy to other radiation chemistry-mass spectra correlations, the 70 eV mass spectrum of CF_3Br is a reasonable indication of the distribution of the ionic species in the radiolysis of CF_3Br , the $G(\text{CF}_3^+)$ value can be readily estimated to be ~ 1.8 . Consequently, if the competing process (Reaction 6) is a relatively unimportant process, the yield of CF_4 could be satisfactorily correlated with the mass spectra data.

However, since the formation of CF_3Br^+ by Reaction 6 represents the transfer of charge from a radical ion to a molecule and would therefore likely be endothermic by perhaps 1 eV, Reaction 5 should be the preferred process and hence represent the principal path of the ionic reaction.

Figure 1. ARRHENIUS PLOT OF CF_4 FORMATION

Our results thus provide direct experimental evidence of the existence of a fluorine atom abstraction reaction by a radiation-produced intermediate, i.e., the CF_3^+ ion, despite the commonly believed inertness of the C-F bond. Such an abstraction reaction, however, is not unique for CF_3Br , and we have also observed similar results in the radiolysis of CF_3Cl , as discussed in Section 3.3.

3.2.3.2. CF_2Br_2 Formation

In contrast to the formation of CF_4 , which is considered to be uniquely due to an ionic mechanism, CF_2Br_2 can, at least in principle, be produced as the result of bromine abstraction by either the CF_2Br^+ ion or the CF_2Br radical, as well as by the interaction of these and other intermediates such as CF_2 with the radiolytically produced Br_2 .

The reaction of a CF_2Br^+ ion with a CF_3Br molecule to eventually form CF_2Br_2 will probably be endothermic, since it necessarily involves a charge transfer between the CF_2Br^+ ion and either a CF_2Br_2 molecule or a $\text{CF}_3\cdot$ radical and therefore may or may not be possible. The reaction of the $\text{CF}_2\text{Br}\cdot$ radical with CF_3Br to form $\text{CF}_2\text{Br}_2\cdot$, on the other hand, involves both the cleavage and the formation of a C-Br bond. This reaction can be expected to be a feasible process, although it requires a positive energy of activation.

The foregoing considerations, we believe, agree with the experimental results: the yield of CF_2Br_2 increased from approximately 1.6 at 27°C to 3.1 at 300°C. A standard Arrhenius plot, as shown in Figure 2, indicates that the activation energy for such a process equals ~ 1 kcal/mole. This value can be compared with the value of 3 to 5 kcal/mole, which was determined by Bowles, Majer, and Ross (ref. 17) for chlorine abstraction by CF_2Cl from 1,3-dichlorotetrafluoroacetone when the latter compound undergoes photochemically induced decomposition.

An approximate material balance could be achieved on the basis of other products that were formed, including C_2F_6 , Br_2 , and occasionally CF_3H . This last product, although apparently unexpected, is similar to the observation of Holmes and Kutschke (ref. 18) that "traces of CF_3H were always found among the products of the photolysis of hexafluoroacetone, apparently due to the reaction between the $\text{CF}_3\cdot$ intermediates with the last traces of residual hydrogenous material in the reaction vessel."

Figure 2. ARRHENIUS PLOT OF CF_2Br_2 FORMATION FROM CF_3Br

3.3. Chlorotrifluoromethane

A study of the radiation chemistry of CF_3Cl was carried out because of its known capability of serving as a radiation-fluorinating agent. Furthermore, for the purpose of providing information on the chemical behavior of the radiation-produced intermediates from the simple fluorocarbons, CF_3Cl also represents an optimal material either from the viewpoint of the availability of pertinent literature or from the viewpoint of practical experimental convenience, e.g., the analytical chemistry of anticipated principal products and the use of radical scavengers for the study of the radiation-produced intermediates.

3.3.1. Experimental

3.3.1.1. Materials and Sample Preparation

CF_3Cl , supplied by Matheson Company, was purified on a vacuum line by bulb-to-bulb distillation coupled with the freezing-pumping and thawing technique. Specifically, two large vessels were attached to a vacuum line and evacuated. The commercial CF_3Cl was diffused into the system and condensed into one vessel that was kept at liquid nitrogen temperature. The noncondensable products were removed by pumping. Then, for six repeated cycles, the material was allowed to thaw and diffuse into the system; this was followed by freezing and pumping. Finally, the middle portion of the material was vacuum-transferred into the evacuated vessel. Gas-chromatographic analysis showed that this material was pure.

Other materials used included Br_2 , Xe, and He. These were either ACS (Br_2) or research-grade materials (Xe, He) and were used without further purification.

The samples were prepared conventionally by using a vacuum manifold system. Since normal cleaning procedures employing cleansing fluids did not produce satisfactory samples, a small amount of CF_3Cl was diffused into an evacuated vessel. A Tesla coil was used to initiate a discharge in order to break the organic coating into smaller molecules and to allow these molecules (or fragments) to react with CF_3Cl . The vessels were then evacuated again by pumping. This procedure was comparatively effective. Irradiation vessels twice treated by this method are usually, though not always, free of contaminating hydrogenous impurities, as indicated by the appearance of CF_3H among the irradiation products of CF_3Cl .

3.3.1.2. Sample Irradiation

Irradiation was carried out by using the IITRI cobalt 60 source at ambient temperature. The radiation dose rate ranged from 2.6×10^{19} to 3.9×10^{19} eV/gram-hour, and total integrated dose from 1.3×10^{20} to 1.9×10^{21} eV/gram.

3.3.1.3. Bromine Determination

Several different methods were tried in order to correlate the optical density measurements with the amount of Br_2 present in the sample. It was found that, as an approximation, the extinction coefficient of Br_2 remains unchanged in CCl_4 solutions. Also, a good calibration curve relating the optical

density to the vapor-phase Br_2 concentration can be obtained simply by dissolving selected amounts of Br_2 in a known volume of CCl_4 and then measuring the optical density on a Beckman DU spectrophotometer.

3.3.1.4. Product Analyses

Analyses of irradiated samples were carried out by using a Burrell K-1 chromatograph. This chromatograph was modified in our laboratory, however, to provide a greaseless injection port and a greaseless sample collector because previous experience had shown that the stopcock grease was responsible for the absorption of a significant fraction of the radiolytic products.

In order to remove the traces of Cl_2 gas produced upon irradiation, mercury was placed in the sample collector. The radiolytic products were separated on a 250-cm-long-high-activity silica gel column, and the column temperature was programmed from 50 to 150°C. The areas of chromatographic peaks were measured with a planimeter.

3.3.2. Results

3.3.2.1. Effect of Total Dose

Experiments on the effects of total dose on the radiolysis of CF_3Cl were carried out at ambient temperature (27°C). The results of these experiments are given in Table 4. Apparently, the $G(\text{CF}_4)$ value remains essentially constant with dose, whereas the $G(\text{CF}_2\text{Cl}_2)$ value decreases with increasing total dose. This result suggests that the radiation stability of the dichloro compound is lower and that secondary reactions occur.

Table 4
EFFECT OF INTEGRATED DOSE^a ON RADIOLYSIS OF CF₃Cl

Total Dose, <u>10²⁰ eV/gram</u>	<u>G(CF₄)</u>	<u>G(CF₂Cl₂)</u>
1.24	2.3 2.2	21.8 25.4
1.49	2.5 2.4	17.8 17.0
2.24	2.0 2.0	- 7.6
5.96	2.4	6.7
6.55	2.0 2.0	11.1 11.4
8.82	1.9 1.7	5.2 5.2
13.4	2.0	7.7
15.9	2.1	4.8
21.8	1.5 1.4	2.3 3.9
22.9	2.2 2.1	5.1 5.4
24.6	2.0 2.1	4.7 4.7
28.7	2.0 2.1	4.2 4.3
34.7	2.0 2.0	3.4 3.5
41.8	2.0 2.1	3.0 2.6
86.9	2.0 2.2	2.7 2.8

^aDose rate was 9.35×10^{18} eV/gram-hour.

3.3.2.2. Effect of Sample Pressure

The effect of CF_3Cl pressure was studied over the range of 127 to 1020 mm Hg. As shown by the results, which are summarized in Table 5, the yield of both CF_4 and CF_2Cl_2 is essentially independent of the sample pressure over an eight-fold change in pressure. Because the formation of either of these products from the unimolecular decomposition of CF_3Cl is inherently impossible, the most probable explanation would be the very high reactivity of the intermediates involved; this deduction agrees with our previous conclusions.

Table 5
EFFECT OF DIFFERENT PRESSURES ON RADIOLYSIS OF CF_3Cl

Pressure, mm Hg	Product ^a	
	G(CF_4)	G(CF_2Cl_2)
1.02×10^3	2.0	2.4
8.02×10^2	1.6	2.1
5.44×10^2	1.9	2.5
2.70×10^2	1.8	2.5
2.58×10^2	1.8	2.5
2.55×10^2	1.9	2.1
1.38×10^2	1.9	2.2
1.27×10^2	1.9	2.0

^aIn addition, small amounts of Cl_2 and C_2F_6 were found in these samples. Irradiation was carried out at ambient temperature at 3.94×10^{19} eV/gram-hour to a total dose of 3.84×10^{21} eV/gram.

The yield of CF_2Cl sometimes can be significantly higher than that of CF_4 . Such a result is entirely in agreement with our interpretation that whereas CF_4 can be formed only by an ionic process from CF_3^+ , both ionic and radical processes could contribute to the observed formation of CF_2Cl_2 .

3.3.2.3. Effect of Added Bromine

Several experiments were carried out to study the effect of added Br_2 on the radiolysis of CF_3Cl . The advantages of such experiments are (1) efficient scavenging of the radiation-produced radical intermediates and hence (2) elimination of possible interference by the last traces of hydrogenous impurities that are extremely difficult to remove from the irradiation vessels.

The results of these experiments are expressed in terms of product yield as a function of $\text{Br}_2:\text{CF}_3\text{Cl}$ ratio and of irradiation time in Tables 6 and 7, respectively. They show that whereas $G(\text{CF}_4)$ remains essentially constant except at rather high $\text{Br}_2:\text{CF}_3\text{Cl}$ ratios, the yield of other products varies significantly with the relative amount of Br_2 present in the sample. As may be expected, $G(\text{CF}_2\text{Cl}_2)$ decreases with increasing $\text{Br}_2:\text{CF}_3\text{Cl}$ ratio, whereas the two Br_2 containing products, CF_3Br and CF_2ClBr , increase with the relative amount of Br_2 present in the system.

Table 6

EFFECT OF ADDED BROMINE ON RADIOLYSIS OF CF_3Cl
AS A FUNCTION OF Br_2 TO CF_3Cl RATIO

Irradiation Time, hr	Ratio of CF_3Cl to Br_2	Yield of Products, G value			
		CF_4	CF_3Br	CF_2Cl_2	CF_2ClBr
23	3	1.4	5.0	-	3.4
23	0.31	2.0	2.1	-	2.9
24	0.085	2.0	1.4	0.16	4.0
24	0.05	2.2	1.8	0.12	3.4
40	1.4	1.8	2.4	-	3.8
40	0.26	1.9	2.9	-	4.0
40	0.029	2.0	2.1	0.7	3.1
40	0.008	2.3	2.9	1.1	1.7
47	1.7	1.8	2.4	-	4.0
44	0.09	2.0	2.0	-	1.1
47	0.08	2.2	2.4	0.15	2.7
47	0.028	2.2	2.7	0.53	3.8
64	0.12	2.9	2.9	0.43	5.1
64	0.04	2.0	1.7	0.40	3.0
90	0.48	1.4	1.6	-	2.1
90	0.29	1.9	2.9	0.16	4.0
94	0.25	1.8	2.7	0.15	4.2
90	0.15	1.9	2.2	0.2	3.2
95	0.01	1.5	1.4	0.69	0.94
103	0.004	2.1	0.7	2.6	1.0
114	3	1.4	3.6	-	2.8
114	0.15	2.1	2.4	0.35	3.7
115	0.20	1.8	2.8	0.22	3.7
136	3	1.5	4.3	-	3.1
154	0.19	2.0	2.3	0.37	3.3
144	0.17	1.9	2.6	0.38	3.8
144	0.15	1.9	2.1	0.30	3.3
136	0.02	2.0	1.9	1.0	0.9
136	0.0036	2.0	1.5	2.4	0.5
186	3	1.8	4.5	0.08	3.7
300	0.024	2.0	2.2	2.3	0.2

Table 7

EFFECT OF ADDED BROMINE ON RADIOLYSIS OF CF_3Cl
AS A FUNCTION OF IRRADIATION TIME

Ratio of CF_3Cl to Br_2	Irradiation Time, hr	Yield of Products, G value			
		CF_4	CF_3Br	CF_2Cl_2	CF_2ClBr
3	6	1.4	2.4	-	-
3	27	1.4	5.0	-	3.4
3	114	1.4	3.6	-	2.8
3	136	1.5	4.3	-	3.1
3	186	1.8	4.5	0.8	3.7
1.4	40	1.8	2.4	-	3.8
1.7	47	1.8	2.4	4.0	-
0.31	23	2.0	2.1	-	2.9
0.48	90	1.4	1.6	-	2.1
0.29	94	1.9	2.9	1.5	4.0
0.2	6	2.5	-	-	-
0.26	40	1.9	2.9	-	4.0
0.25	94	1.8	2.7	0.15	4.2
0.20	115	1.8	2.8	0.22	3.7
0.15	90	1.9	2.2	0.2	3.2
0.15	114	2.1	2.4	0.35	3.7
0.17	144	1.9	2.6	0.38	3.8
0.15	144	1.9	2.1	0.30	3.3
0.19	154	2.0	2.3	0.37	3.3
0.12	64	2.9	2.9	0.43	5.0
0.10	15	1.9	2.1	-	4.4
0.085	24	2.0	1.4	0.16	4.0
0.091	44	2.0	2.0	-	1.1
0.081	47	2.2	2.4	0.15	2.7
0.05	24	2.2	1.8	0.12	3.4
0.043	64	2.0	1.7	0.40	3.0
0.029	40	2.0	2.1	0.7	3.1
0.028	47	2.2	2.7	0.53	3.8
0.021	136	2.0	1.9	1.0	0.90
0.024	300	2.0	2.2	2.3	0.21
0.009	15	2.2	1.8	0.8	3.0
0.008	40	2.3	2.9	1.1	1.7
0.010	95	1.5	1.4	0.7	0.9
0.004	103	2.1	0.7	2.6	1.0
0.0036	136	2.0	1.5	2.4	0.5

3.3.2.4. Effect of Rare Gases

The results of studies on the effect of the rare gases Xe and He on the radiolysis of CF_3Cl are shown in Table 8. Within the limits of experimental accuracy, the effect on the $\text{G}(\text{CF}_4)$ yield is negligible, but $\text{G}(\text{CF}_2\text{Cl}_2)$ increases significantly when the concentration of He in the CF_3Cl sample is on the order of 1 to 4%.

Table 8

EFFECT OF XENON AND HELIUM ON RADIOLYSIS OF CF_3Cl ^a

<u>Moles of CF_3Cl</u>	<u>Moles of Gas</u>	<u>$\text{G}(\text{CF}_4)$</u>	<u>$\text{G}(\text{CF}_2\text{Cl}_2)$</u>
<u>Xenon</u>			
5.01×10^{-4}	1.71×10^{-6}	2.7	2.0
5.01×10^{-4}	1.65×10^{-6}	2.4	2.0
4.07×10^{-4}	0.80×10^{-6}	2.2	2.3
4.06×10^{-4}	7.73×10^{-6}	2.1	2.3
4.90×10^{-4}	18.96×10^{-6}	2.2	2.3
5.00×10^{-4}	14.84×10^{-6}	2.3	2.3
<u>Helium</u>			
4.15×10^{-4}	1.73×10^{-6}	2.2	2.0
4.13×10^{-4}	1.72×10^{-6}	2.3	3.2
4.28×10^{-4}	5.47×10^{-6}	1.7	3.2
4.19×10^{-4}	5.35×10^{-6}	1.7	3.2
4.06×10^{-4}	10.42×10^{-6}	2.2	3.7
4.14×10^{-4}	14.70×10^{-6}	2.4	3.4

^aSamples were irradiated at a dose rate of 2.73×10^{19} ev/gram-hour to a total dose of 4.55×10^{21} ev/gram.

3.3.3. Process Mechanism Considerations

Both ionic and radical mechanisms, we believe, contribute to the chemical processes observed in the radiolysis of CF_3Cl . Specifically, the results of our experimental studies, supplemented by mass spectrometric data,* indicate that the principal intermediates must be, in approximate order of abundance, $\text{CF}_3^\cdot$, CF_3^+ , $\text{CF}_2\text{Cl}^\cdot$, and CF_2Cl^+ .

The CF_3 radicals are reactive and capable of (1) efficiently abstracting hydrogen atoms from hydrogenous materials, (2) reacting with halogen molecules to form F_3CH or the trifluoromethyl halides, (3) combining with each other to form molecules of C_2F_6 , or (4) undergoing addition reactions to the C-C bond. On the other hand, in analogy to the CF_3Br system, these radicals are not expected to abstract fluorine atoms to form CF_4 . Asycough and Steacie (ref. 13), for example, photolyzed hexafluoroacetone over the temperature range 25 to 350°C and did not observe CF_4 among the products of photolysis. Their findings agree with the results of a subsequent study carried out by Gordon (ref. 14). Consequently, only the interaction of the radiation-produced CF_3^+ ions with other fluorine-containing species, principally CF_3Cl , is believed to contribute to the observed CF_4 formation.

*The 70-eV mass spectrum of CF_3Cl is: CF_3^+ , 100; CF_2Cl^+ , 23.7; CF_2^+ , 6.4; Cl^+ , 4.1; CF^+ , 1.8; and CF_3Cl^+ , 0.7.

Both the CF_2Cl^+ ions produced in the above process and those formed directly as the result of the interaction of CF_3Cl molecules with radiation should be able to abstract atomic chlorine from CF_3Cl molecules to eventually form molecules of CF_2Cl_2 . Similarly, at least some, if not all, of the $\text{CF}_2\text{Cl}\cdot$ radicals may also be precursors for this compound, as evidenced by the formation of CF_2Cl observed by Bowles et al (ref. 17) in the photolysis of 1,3-dichlorotetrafluoroacetone. In particular, it is interesting to note that the yield of CF_2Cl_2 was higher when ultraviolet radiation of shorter wavelength was used in the photolysis experiment. This result suggests that $\text{CF}_2\text{Cl}\cdot$ radicals at higher energy states, as may have been formed in our radiation experiments, would be particularly effective in the chlorine abstraction reaction.

On the basis of the foregoing considerations, the reactions involved in the radiolysis of CF_3Cl and $\text{CF}_3\text{Cl} + \text{Br}_2$ systems would be:

An analysis of the process kinetics can now be made.

3.3.3.1. CF_4 Formation

According to the reaction mechanism outlined above, CF_4 is formed by the interaction of CF_3^+ with CF_3Cl . CF_3^+ is formed either by the direct interaction of radiation with CF_3Cl or by the reaction of CF_2Cl^+ with CF_3Cl . In turn, CF_2Cl^+ can also be produced directly by radiation or from the reaction of CF_3^+ with CF_3Cl . Consequently,

$$\frac{d[\text{CF}_3^+]}{dt} = a + k_{17}[\text{CF}_2\text{Cl}^+][\text{CF}_3\text{Cl}] - \left\{ k_2[\text{Br}_2] + k_{15}[\text{CF}_3\text{Cl}] \right\} [\text{CF}_3^+]$$

$$\frac{d[\text{CF}_2\text{Cl}^+]}{dt} = b + k_{15}[\text{CF}_3^+][\text{CF}_3\text{Cl}] - \left\{ k_3[\text{CF}_3\text{Cl}] + k_{18}[\text{Br}_2] \right\} [\text{CF}_2\text{Cl}^+]$$

At steady state conditions:

$$[\text{CF}_3^+] = \frac{a + k_{17}[\text{CF}_3\text{Cl}][\text{CF}_2\text{Cl}^+]}{k_{16}[\text{Br}_2] + k_{15}[\text{CF}_3\text{Cl}]}$$

$$[\text{CF}_2\text{Cl}^+] = \frac{b + k_{15}[\text{CF}_3^+][\text{CF}_3\text{Cl}]}{k_{17}[\text{CF}_3\text{Cl}] + k_{18}[\text{Br}_2]}$$

$$\begin{aligned}
\text{CF}_3^+ &= \frac{1}{k_{15}[\text{Br}_2] + k_{15}[\text{CF}_3\text{Cl}]} \\
&\quad \left\{ a + \frac{k_{17}[\text{CF}_3\text{Cl}]}{k_{17}[\text{CF}_3\text{Cl}] + k_{18}[\text{Br}_2]} \left(b + k_{15}[\text{CF}_3^+][\text{CF}_3\text{Cl}] \right) \right\} \\
&= \frac{1}{k_{16}[\text{Br}_2] + k_{15}[\text{CF}_3\text{Cl}]} \left\{ a + \frac{b}{1 + \frac{k_{18}}{k_{17}} R} + \frac{k_{15}[\text{CF}_3^+][\text{CF}_3\text{Cl}]}{1 + \frac{k_{18}}{k_{17}} R} \right\} \\
&= \left(\frac{1}{k_{16}[\text{Br}_2] + k_{15}[\text{CF}_3\text{Cl}]} \right) \left(a + \frac{b}{1 + \frac{k_{18}}{k_{17}} R} \right) \\
&\quad + \left(\frac{k_{15}[\text{CF}_3\text{Cl}]}{k_{16}[\text{Br}_2] + k_{15}[\text{CF}_3\text{Cl}]} \right) \left(\frac{[\text{CF}_3^+]}{1 + \frac{k_{18}}{k_{17}} R} \right)
\end{aligned}$$

where $R = [\text{Br}_2]/[\text{CF}_3\text{Cl}]$.

When R is very small,

$$\begin{aligned}
\frac{d[\text{CF}_4]}{dt} &= k_{15}[\text{CF}_3^+][\text{CF}_3\text{Cl}] \\
&= \left(\frac{1}{1 + \frac{k_{16}}{k_{15}} R} \right) \left(a + \frac{b}{1 + \frac{k_{18}}{k_{17}} R} \right) + \left(\frac{1}{1 + \frac{k_{16}}{k_{15}} R} \right) \left(\frac{d[\text{CF}_4]/dt}{1 + \frac{k_{18}}{k_{17}} R} \right) \\
&= a + b + \frac{d[\text{CF}_4]}{dt}
\end{aligned}$$

When R approaches zero,

$$\frac{d[\text{CF}_4]}{dt} \approx \frac{a + b}{2}$$

When R is very large,

$$\frac{d[\text{CF}_4]}{dt} \rightarrow 0 \text{ (a trivial case)}$$

For intermediate values of R,

$$\frac{d[\text{CF}_4]}{dt} = \frac{a + \frac{b}{\left(1 + \frac{k_{18}}{k_{17}} R\right)}}{1 + \frac{k_{16}}{k_{15}} R - \frac{1}{\left(1 + \frac{k_{18}}{k_{17}} R\right)}}$$

Consequently, $d[\text{CF}_4]/dt$ should decrease monotonically with increasing R. Furthermore, if it can be assumed that

$k_{16} \approx k_{15} \approx k_{17}$ (i.e., assuming that these reactions occur on each collision and that the collision cross sections of Br_2 and CF_3Cl_3 are comparable), then

$$\begin{aligned} \frac{d[\text{CF}_4]}{dt} &= \frac{a + \frac{b}{1 + R}}{1 + R - \frac{1}{1 + R}} \\ &= \frac{a}{1 + R} + \frac{b}{(1 + R)^2} \\ &= a X_{\text{CF}_3\text{Cl}} + b X_{\text{CF}_3\text{Cl}}^2 \\ &\approx a X_{\text{CF}_3\text{Cl}} \end{aligned}$$

since $1/(1 + R) = X_{\text{CF}_3\text{Cl}}$ and since $b X_{\text{CF}_3\text{Cl}} \ll a$, as may be expected on the basis of mass spectral data. However, since only the interaction of radiation with the CF_3Cl molecules is believed to be responsible for the observed change and since the secondary electrons from the walls of the vessel probably contribute the majority of the absorbed dose, an additional correction, $X_{e,\text{CF}_3\text{Cl}}$, reflecting the electron fraction of CF_3Cl , should be made, i.e.,

$$G \cong a X_{\text{CF}_3\text{Cl}} X_{e,\text{CF}_3\text{Cl}}$$

3.3.3.2. CF_3Br Formation

The reaction of Br_2 with CF_3^+ and the reaction of Br_2 with $\text{CF}_3\cdot$ are both believed to be responsible for CF_3Br formation according to the postulated mechanism. In this connection, both CF_3^+ and CF_3 can be formed either by the direct interaction of radiation with the CF_3Cl molecules or by the interaction of CF_2Cl^+ with other molecules of CF_3Cl . Furthermore, CF_2Cl^+ also can be formed either as a primary radiation chemical product or from the interaction of CF_3^+ with CF_3Cl .

Although our experimental results cannot justify a detailed kinetic treatment, it is nevertheless possible and worthwhile to examine the experimental data on the basis of the postulated mechanism.

By using the derivations in Section 3.3.3.1.,

$$[CF_3^+] = \frac{\frac{1}{k_{16}[Br_2] + k_{15}[CF_3Cl]} \left\{ a + \frac{b}{1 + \frac{k_{18}}{k_{17}} R} \right\}}{\left\{ 1 - \frac{1}{\left(1 + \frac{k_{16}}{k_{15}} R \right) \left(1 + \frac{k_{18}}{k_{17}} R \right)} \right\}}$$

where $R = Br_2/CF_3Cl$. Similarly, the corresponding set of equations for the $CF_3^\bullet$ radical is:

$$\frac{d[CF_3^\bullet]}{dt} = c + d \frac{k_{20}[CF_3Cl]}{k_{20}[CF_3Cl] + k_{21}[Br_2]} - k_{19}[CF_3^\bullet][Br_2]$$

and

$$[CF_3^\bullet] = \frac{1}{k_{19}[Br_2]} c + \left(\frac{d}{1 + \frac{k_{21}}{k_{20}} R} \right)$$

Consequently,

$$\begin{aligned} \frac{d[CF_3Br]}{dt} &= k_{16}[CF_3^+][Br_2] + k_{19}[CF_3^\bullet][Br_2] \\ &= \frac{\frac{1}{1 + \frac{k_{15}}{k_{16}} R} \left(a + \frac{b}{1 + \frac{k_{18}}{k_{17}} R} \right)}{\left\{ 1 - \frac{1}{\left(1 + \frac{k_{16}}{k_{15}} R \right) \left(1 + \frac{k_{18}}{k_{17}} R \right)} \right\}} + \left(c + \frac{d}{1 + \frac{k_{21}}{k_{20}} R} \right) \end{aligned}$$

$$\begin{aligned}
&= \frac{\frac{k_2}{k_1} R \left\{ \left(1 + \frac{k_{18}}{k_{17}} R \right) a + b \right\}}{\frac{k_{16}}{k_{15}} R + \left(\frac{k_{18}}{k_{17}} \frac{k_{18}}{k_{19}} \right) R^2} + c + \frac{d}{1 + \frac{k_{21}}{k_{20}} R} \\
&= \frac{\left(1 + \frac{k_{18}}{k_{19}} R \right) a + b}{1 + \left(\frac{k_{18}}{k_{17}} \right) \left(\frac{k_{15}}{k_{16}} \right) + \frac{k_{18}}{k_{17}} R} + \frac{c + d}{1 + \frac{k_{21}}{k_{20}} R}
\end{aligned}$$

Consequently, if $k_{18} \approx k_{17}$ and $k_{15} \approx k_{16}$, as $R \rightarrow 0$,

$$\frac{d[\text{CF}_3\text{Br}]}{dt} = \frac{a + b}{2} + c + d$$

Interestingly, the value of $d[\text{CF}_3\text{Br}]/dt$ is expected to decrease initially with increasing bromine concentration due to its large effect on the d term. At higher values of R , however, the d term becomes negligible, and the variation of $d[\text{CF}_3\text{Br}]/dt$ with R should be slow. (At very large values of R , the value of $d[\text{CF}_3\text{Br}]/dt$ approaches $a + c$.) This conclusion, as shown in Tables 9 and 10, indeed agrees with the experimental data.

3.3.3.3. CF_2ClBr Formation

Reactions 4 and 7, which are responsible for CF_2ClBr formation, require either CF_2Cl^+ or CF_2Cl as the intermediate. According to our postulated mechanism, $\text{CF}_2\text{Cl}\cdot$ can be formed only directly by the radiolysis of CF_3Cl , whereas CF_2Cl^+ can be produced either by the direct interaction of CF_3Cl with radiation,

or the interaction of CF_3^+ with CF_3Cl . By using the equations developed in Section 3.3.3.1. for CF_4 formation,

$$[\text{CF}_2\text{Cl}^+] = \frac{1}{k_{17}[\text{CF}_3\text{Cl}] + k_{18}[\text{Br}_2]} \left(b + \frac{a}{1 + \frac{k_{16}}{k_{15}} R} \right) \left\{ 1 - \frac{1}{\left(1 + \frac{k_{16}}{k_{15}} R \right) \left(1 + \frac{k_{18}}{k_{17}} R \right)} \right\}^{-1}$$

Consequently, the production of CF_2ClBr from CF_2Cl^+ can be described by the following equation:

$$\frac{d_+[\text{CF}_2\text{ClBr}]}{dt} = k_{18}[\text{CF}_2\text{Cl}^+][\text{Br}] = \frac{\frac{1}{1 + \frac{k_{17}}{k_{18}} R} \left(b + \frac{a}{1 + \frac{k_{16}}{k_{15}} R} \right)}{1 - \frac{1}{\left(1 + \frac{k_{16}}{k_{15}} R \right) \left(1 + \frac{k_{18}}{k_{17}} R \right)}}$$

The component due to the radical intermediate $\text{CF}_2\text{Cl}\cdot$ is simpler:

$$\frac{d[\text{CF}_2\text{Cl}\cdot]}{dt} = d - k_{20}[\text{CF}_2\text{Cl}\cdot][\text{CF}_3\text{Cl}] + k_{21}[\text{CF}_2\text{Cl}\cdot][\text{Br}_2]$$

$$[\text{CF}_2\text{Cl}\cdot] = \frac{d}{k_{20}[\text{CF}_3\text{Cl}] + k_{21}[\text{Br}_2]}$$

and

$$\frac{d_R[\text{CF}_2\text{ClBr}]}{dt} = k_{21}[\text{CF}_2\text{Cl}\cdot][\text{Br}_2] = \frac{d}{1 + \frac{k_{20}}{k_{21}}}$$

By combining the ionic and radical yields,

$$\begin{aligned} \frac{d[\text{CF}_2\text{ClBr}]}{dt} &= \frac{d_+[\text{CF}_2\text{ClBr}]}{dt} + \frac{d_-[\text{CF}_2\text{ClBr}]}{dt} \\ &= \frac{\frac{1}{1 + \frac{k_{17}}{k_{18}} R} \left(b + \frac{a}{1 + \frac{k_{16}}{k_{15}} R} \right)}{1 - \frac{1}{\left(1 + \frac{k_{16}}{k_{15}} R \right) \left(1 + \frac{k_{18}}{k_{17}} R \right)}} + \frac{d}{1 + \frac{k_{20}}{k_{21}} R} \end{aligned}$$

If R is very large, the above equation reduces to

$$\frac{d[\text{CF}_2\text{ClBr}]}{dt} = b + d$$

If R is very small,

$$\frac{d[\text{CF}_2\text{ClBr}]}{dt} = \frac{a + b}{1 + \frac{k_{16}}{k_{15}} \frac{k_{17}}{k_{18}}} = \frac{1}{2} (a + b)$$

At intermediate but small values of R ($R < 1$), $d[\text{CF}_2\text{ClBr}]/dt$ is expected to vary, but slowly.

An interesting observation is that in order for the above results to agree qualitatively with the experimental data, d, i.e., the primary $\text{CF}_2\text{Cl}\cdot$ radical yield, will have to be large.

Since, however, the $\text{CF}_2\text{Cl}\cdot$ species is believed to be able to react only according to Reactions 6 and 7, it follows that at extremely low R values, where the d term in the $d[\text{CF}_2\text{ClBr}]/dt$ equation becomes negligible, we should expect a substantial increase in the CF_2Cl_2 yield. This is indeed in agreement with the radiolysis results.

3.3.3.4. CF_2Cl_2 Formation

According to our mechanism, CF_2Cl_2 can be formed either through Reaction 3 or 6. By using the results obtained earlier for the steady-state concentrations of the intermediates involved,

$$\begin{aligned}
 \frac{d[\text{CF}_2\text{Cl}_2]}{dt} &= k_{17}[\text{CF}_2\text{Cl}^+][\text{CF}_3\text{Cl}] + k_{20}[\text{CF}_2\text{Cl}\cdot][\text{CF}_3\text{Cl}] \\
 &= \frac{\left(\frac{k_{17}[\text{CF}_3\text{Cl}]}{k_{17}[\text{CF}_3\text{Cl}] + k_{18}[\text{Br}_2]} \right) \left(b + \frac{a}{1 + \frac{k_{16}}{k_{15}} R} \right)}{1 - \frac{1}{\left(1 + \frac{k_{16}}{k_{15}} R \right) \left(1 + \frac{k_{18}}{k_{17}} R \right)}} \\
 &\quad + \frac{k_{20}[\text{CF}_3\text{Cl}]d}{k_{20}[\text{CF}_3\text{Cl}] + k_{21}[\text{Br}_2]} \\
 &= \frac{\frac{1}{1 + \frac{k_{18}}{k_{19}} R} \left(b + \frac{a}{1 + \frac{k_{16}}{k_{15}} R} \right)}{1 - \frac{1}{\left(1 + \frac{k_{16}}{k_{15}} R \right) \left(1 + \frac{k_{18}}{k_{17}} R \right)}} + \frac{d}{1 + \frac{k_{21}}{k_{20}} R} \\
 &= \frac{1}{R} \left[\frac{\left(1 + \frac{k_{16}}{k_{15}} R \right) b + a}{\frac{k_{16}}{k_{15}} + \frac{k_{18}}{k_{17}} + \left(\frac{k_{16}}{k_{15}} \frac{k_{18}}{k_{17}} \right) R} \right] + 1 + \frac{k_{21}}{k_{20}} R
 \end{aligned}$$

Thus, if the bromine concentration is high, $d[\text{CF}_2\text{Cl}_2]/dt$ approaches zero. As the bromine concentration decreases, the value of $d[\text{CF}_2\text{Cl}_2]/dt$ should increase monotonically. At very low R values, the function for CF_2Cl_2 formation becomes

$$\frac{d[\text{CF}_2\text{Cl}_2]}{dt} = \frac{a + b}{\left(\frac{k_{16}}{k_{15}} + \frac{k_{18}}{k_{17}}\right)} \frac{[\text{CF}_3\text{Cl}]}{[\text{Br}_2]} + d$$

and should therefore be able to assume very large values. This conclusion is also in agreement with the experimental results.

3.4. Carbon Tetrafluoride

A limited number of experiments designed to study the radiation chemistry of carbon tetrafluoride was carried out in the earlier phases of this program. Specifically, these experiments included the radiolysis of pure CF_4 , $\text{CF}_4 + \text{Br}_2$, and $\text{CF}_4 + \text{Cl}_2$.

3.4.1. Experimental

3.4.1.1. Materials and Sample Preparation

Commercial CF_4 (Freon-14) was purified by the preferential removal of the higher-boiling impurities through the use of a silica gel column. Other materials, which included ACS-grade bromine and reagent-grade chlorine, were used without further purification.

The samples were prepared by means of a vacuum manifold system, as described previously in Section 3.3.1.1.

3.4.1.2. Irradiation and Analysis

Irradiation was carried out by using the IITRI cobalt 60 source at ambient temperature. The dose rates in these experiments ranged from 2.5×10^{19} to 3.9×10^{19} eV/gram-hour, and the integrated doses were from 1.7×10^{21} to 3.9×10^{21} eV/gram.

Analyses of the samples were carried out by using a Burrell K-1 chromatograph. In the case of the samples containing Cl_2 , this species was removed by successive treatment with sodium hydroxide, silver powder, and mercury. In the case of the samples containing Br_2 , analyses of the radiolytic products were satisfactorily carried out by using a 250-cm-long silica gel column and careful stepwise temperature-programming.

3.4.2. Results

The results of the CF_4 radiolysis experiments, summarized in Table 9, show that in the absence of the free halogens, the principal product is C_2F_6 , with $G(\text{C}_2\text{F}_6) \cong 2$. The addition of free Br_2 reduced $G(\text{C}_2\text{F}_6)$ to $\cong 1$ and was accompanied by the formation of CF_3Br with $G(\text{CF}_3\text{Br}) = 3$ to 5. The addition of free Cl_2 led to the formation of CF_3Cl with $G(\text{CF}_3\text{Cl}) \cong 0.35$ and completely suppressed the formation of C_2F_6 .

3.4.3. Process Mechanism Considerations

Although a quantitative treatment of the CF_4 radiolysis results is not justified on the basis of the available data, the following conclusions concerning the radiation chemistry of CCl_4 in a gaseous system can nevertheless be made.

Table 9

RADIOLYSIS OF CF_4 , $\text{CF}_4 + \text{Br}_2$, AND $\text{CF}_4 + \text{Cl}_2$

Sample	Dose, eV/gram	$G(\text{C}_2\text{F}_6)$	$G(\text{CF}_3\text{Br})$	$G(\text{CF}_3\text{Cl})$	Remarks
CF_4	3.5×10^{21}	2.0	-	-	Average of 10 experiments
$\text{CF}_4 + \text{Br}_2$ (5:2)	1.9×10^{21}	1.0	4.0	-	
$\text{CF}_4 + \text{Br}_2$ (5:2)	3.9×10^{21}	1.6	2.6	-	
$\text{CF}_4 + \text{Br}_2$ (3:2)	1.7×10^{21}	1.0	3.9	-	
$\text{CF}_4 + \text{Br}_2$ (3:2)	1.9×10^{21}	1.0	4.2	-	Average of 2 experiments
$\text{CF}_4 + \text{Br}_2$ (1:1.2)	1.7×10^{21}	0.85	4.7	-	
$\text{CF}_4 + \text{Br}_2$ (1:3)	1.7×10^{21}	0.65	5.0	-	
$\text{CF}_4 + \text{Cl}_2$ (1:1)	3.5×10^{21}	-	0.35	-	Average of 2 experiments

According to mass spectral data, the principal ionic species formed as the result of the interaction of 70-eV electrons with CF_4 are: CF_3^+ , 100; CF_2^+ , 11.8; CF^+ , 6.7; and F^+ , 5.1. Consequently, if these relative abundances also approximately describe the distribution of the ionic species in an irradiated CF_4 sample, the primary yields of the CF_3^+ and CF_2^+ ions would be on the order of 2.5 and 0.3, respectively. Furthermore, on the basis of purely structural and energetic considerations, the primary yields of the radical intermediates can also be expected to be comparable; i.e., the combined primary yields of the CF_3 ions and radicals should be on the order of 4 to 6, whereas those for the CF_2 ions and radicals should be on the order of 1.

In the absence of other reagents, combination reactions (Reactions 22 through 25) and reactions between the probably highly reactive CF_2^+ ions or CF_2 radicals with CF_4 molecules (Reactions 26 and 27) must predominate, leading thereby to the observed predominant formation of C_2F_6 .

In the presence of Br_2 , combinations of the $\text{CF}_3\cdot$ species are completely suppressed, and, instead, CF_3Br is produced through the interaction of these species with Br_2 . The reactions of the CF_2 species with CF_4 , on the other hand, would be considerably more efficient and thus are not affected by the presence of Br_2 except through the competition between the interactions of these species with CF_4 and their interactions with Br_2 . Apparently, Cl_2 , as a more reactive compound, can compete more effectively for reactions with either CF_2^+ and $\text{CF}_2\cdot$, and as a result, the yield of C_2F_6 becomes negligible for the $\text{CF}_4 + \text{Cl}_2$ system.

4. RADIATION SYNTHESIS STUDIES

4.1. The Benzene-Trifluorobromomethane System

A study of the process variable kinetics and the mechanism of the radiation-induced fluorination of aromatic compounds was carried out on the $\text{C}_6\text{H}_6\text{-CF}_3\text{Br}$ system. This system was selected because of the information gained in the radiation chemistry studies of CF_3Br and because of the relationship of the results from such studies with those obtained in similar investigations.

4.1.1. Experimental

4.1.1.1. Materials and Sample Preparation

The CF_3Br used in our experiments was purified as described previously. C_6H_6 was ACS-grade material and was used without further purification.

The preparation of the samples was carried out conventionally by using a vacuum manifold system as described in Section 3.3.1.1.

4.1.1.2. Irradiation and Analysis

Irradiations were carried out in the IITRI hot-cell facility. Gas-chromatographic analyses were carried out by using a dinonyl phthalate column.

4.1.2. Results

The results of these studies are shown in Table 10. Both C_6H_5F and $C_6H_5CF_3$ were produced by the radiolytic process. Over the temperature range studied (27 to 339°C) the yield of C_6H_5F increased slowly with temperature. The yield of $C_6H_5CF_3$, on the other hand, increased initially with temperature but decreased noticeably at 300°C.

Experiments involving $CF_3Br-C_6H_6$ -Xe mixtures at various temperatures were also carried out. The results of these experiments are given in Table 11. Within the limits of experimental accuracy, the results are similar to those obtained for the $CF_3Br-C_6H_6$ system.

4.1.3. Process Mechanism Considerations

The experimentally observed formation of $C_6H_5CF_3$ and C_6H_5F from the radiolysis of $CF_3Br-C_6H_6$ mixtures, we believe, must be principally a result of the interaction of the radiation-produced fluorine-containing intermediates with molecular C_6H_6 and not a result of the interaction of any of the intermediates produced from C_6H_6 with a CF_3Br molecule. As previously

Table 10

RADIOLYSIS OF $\text{CF}_3\text{Br}-\text{C}_6\text{H}_6$ (4:1) MIXTURES

Temp., °C	Radiation Dose, 10^{21} eV/gram	G Values	
		$\text{C}_6\text{H}_5\text{CF}_3$	$\text{C}_6\text{H}_5\text{F}$
26	1.81	2.0	0.22
26	1.81	1.9	0.21
26	1.81	2.0	0.22
26	1.81	2.2	0.22
59 ± 3	1.83	2.1	0.41
59 ± 3	1.83	2.0	0.34
59 ± 3	1.83	1.2	0.21
115 ± 5	1.82	1.9	0.32
115 ± 5	1.82	1.9	0.87
115 ± 5	1.82	2.0	0.41
115 ± 5	1.82	1.8	0.28
120	1.83	2.4	0.30
120	1.83	1.8	0.20
121 ± 5	1.82	2.0	0.29
121 ± 5	1.82	1.9	0.25
121 ± 5	1.82	2.0	0.38
121 ± 5	1.82	2.1	0.36
140 ± 5	1.83	2.1	0.57
140 ± 5	1.83	2.1	0.63
160 ± 7	1.84	2.1	0.80
160 ± 7	1.84	2.2	0.75
160 ± 7	1.84	2.1	0.56
160 ± 7	1.84	2.3	0.98
160 ± 7	1.84	2.2	0.70
180 ± 5	1.80	2.6	1.24
180 ± 5	1.80	2.5	1.34
180 ± 5	1.83	2.1	1.09
180 ± 5	1.83	2.4	1.24
180 ± 5	1.83	2.5	1.34
180 ± 5	1.83	2.7	1.23
180 ± 5	1.83	2.2	1.14
250 ± 10	1.82	1.54	1.41
250 ± 10	1.81	1.7	1.41
250 ± 10	1.81	1.9	1.36
250 ± 10	1.81	1.8	1.54
250 ± 10	1.81	1.6	1.33
339 ± 10	1.82	1.9	1.47

Table 11

RESULTS OF RADIOLYSIS
OF $\text{CF}_3\text{Br}-\text{C}_6\text{H}_6$ -Xe MIXTURES^a

Temp., °C	G Values	
	$\text{C}_6\text{H}_5\text{CF}_3$	$\text{C}_6\text{H}_5\text{F}$
26	2.1	0.26
	2.1	0.27
	2.0	0.27
	2.7	0.36
	2.2	0.29
120	1.8	0.73
	1.7	0.67
160	2.1	0.52
	2.3	0.53
	2.8	0.64
	3.0	0.89
200	2.8	1.8
	2.4	1.4
	1.9	1.2
	2.4	1.3
250	2.5	1.3
	3.1	1.9
300	2.2	1.7
	2.8	2.0
	1.8	1.2

^aIntegrated dose was
1.85 x 10²¹ ev/gram.

indicated, the fluorocarbon bond has been shown to be inert toward free radical attack. On the other hand, studies on the effect of the fluorocarbon:aromatic ratio lead to the conclusion that only the fluorine-containing intermediates are responsible for the observed formation of the fluorinated aromatic product. Interactions between appropriate radicals, e.g., $\text{CF}_3\cdot$ and $\text{C}_6\text{H}_5\cdot$, can, of course, also lead to the formation of the observed products. However, such reactions represent only relatively improbable processes under the conditions of our experiments because of the low radical concentrations expected in a gamma-irradiated system.

The experimental data in Table 11 show that whereas the $G(\text{C}_6\text{H}_5\text{F})$ value increases monotonically with temperature from 26 to 250°C, the effect of temperature on the $G(\text{C}_6\text{H}_5\text{CF}_3)$ value is considerably more complex. Specifically, the $G(\text{C}_6\text{H}_5\text{CF}_3)$ value remains essentially constant from 26 to 140°C, increases with further increase in temperature, and apparently reaches a maximum, but decreases again at higher temperature. The $G(\text{C}_6\text{H}_5\text{CF}_3)$ value becomes lower at 250 to 339°C than at room temperature. Consequently, even though one single process might suffice to describe the radiolytic formation of $\text{C}_6\text{H}_5\text{F}$, several reaction mechanisms must be responsible for the radiation-induced formation of $\text{C}_6\text{H}_5\text{CF}_3$ from the $\text{CF}_3\text{Br}-\text{C}_6\text{H}_6$ system.

On the basis of mass spectrometric data and available literature information on the chemical behavior of $\text{CF}_3\cdot$ radicals, both ionic and radical processes must be capable of contributing

to $C_6H_5CF_3$ formation. On the other hand, a radical mechanism must be principally responsible for the observed formation of C_6H_5F because of the negligible abundance of F^+ ions in the 70-EV mass spectrum of CF_3Br . On the basis of the photochemical studies of Charles and co-workers (ref. 19) the reaction mechanism for $C_6H_5CF_3$ formation from CF_3 radicals and molecular C_6H_6 is believed to proceed through the addition of a CF_3 radical to a C_6H_6 double bond to form the new radical intermediate $C_6H_6CF_3\cdot$ (Reaction 28), and the subsequent hydrogen abstraction reaction by the interaction of the radical intermediate with another radical species, e.g., CF_3 or H (Reaction 29).

In analogy to the results of Stefani and Szwarc (ref. 20) in their radical affinity studies, Reaction 28 can be expected to be the rate-determining step with a positive energy of activation, whereas Reaction 29 would represent a fast process with no significant contribution to the activation energy of the overall process. Consequently, if both CF_3^+ and $CF_3\cdot$ radicals contribute to the observed formation of $C_6H_5CF_3$, a

temperature-dependent process would be superimposed on that of the temperature-independent process and lead to the observed enhancement of $C_6H_5CF_3$ yield at temperatures above $120^\circ C$.

The decrease in $C_6H_5CF_3$ yield at higher temperatures, we believe, can be explained on the basis of the possibility of redissociation of the $[C_6H_6CF_3]^\cdot$ and $[C_6H_6CF_3]^+$ intermediates to the original reactants, i.e., C_6H_6 , $CF_3^\cdot$, and CF_3^+ . An analogy for such a possibility is found in the reaction of photochemically produced trifluoromethyl radicals with C_6H_6 , in which a small fraction of the $[C_6H_6CF_3]^\cdot$ adduct seems to decompose to $CF_3^\cdot$ and C_6H_6 as the temperature was elevated to approximately $150^\circ C$ (ref. 21).

On the basis of the foregoing considerations, the reactions involved in the radiolytic formation of $C_6H_5CF_3$ from $CF_3Br-C_6H_6$ mixtures can be written as:

where g_i and g_r indicate the 100-EV yields of the CF_3^+ and $CF_3\cdot$ intermediates from the radiolysis of CF_3Br ; and $R\cdot$ and A^- are generic representations of all of the radical and negative species in the irradiated system.

Furthermore,

$$\frac{d[C_6H_5CF_3]}{dt} = \frac{d[C_6H_5CF_3]}{dt} R + \frac{d[C_6H_5CF_3]}{dt} I$$

i.e., the radical and ionic processes are considered, as a first approximation, independent of each other. On this basis,

$$\frac{d[C_6H_6CF_3\cdot]}{dt} = k_{31}[CF_3\cdot][C_6H_6] - k_{32}[C_6H_6CF_3\cdot] - k_{33}[C_6H_6CF_3\cdot]$$

At steady state,

$$\frac{d[C_6H_6CF_3\cdot]}{dt} = 0$$

Consequently,

$$C_6H_6CF_3\cdot = \frac{k_{31}[CF_3\cdot][C_6H_6]}{k_{32} + k_{33} R\cdot}$$

and

$$\begin{aligned} \left(\frac{d[C_6H_5CF_3]}{dt} \right) R &= k_{33}[C_6H_6CF_3\cdot][R\cdot] \\ &= \frac{k_{33}[R\cdot]k_{31}[CF_3\cdot][C_6H_6]}{k_{32} + k_{33}[R\cdot]} \\ &= \frac{k_{31}[CF_3\cdot][C_6H_6]}{1 + \frac{k_{32}}{k_{33}}[R\cdot]} \end{aligned}$$

Similarly,

$$\left(\frac{d[C_6H_5CF_3]}{dt} \right)_I = k_{36} [C_6H_6CF_3^+] [A^-]$$

$$\frac{d[C_6H_6CF_3^+]}{dt} = k_{34} [CF_3^+] [C_6H_6] - k_{35} [C_6H_6CF_3^+] - k_{36} [C_6H_6CF_3^+] [A^-]$$

$$[C_6H_6CF_3^+] = \frac{k_{34} [CF_3^+] [C_6H_6]}{k_{35} + k_7 [A^-]}$$

and

$$\left(\frac{d[C_6H_5CF_3]}{dt} \right)_I = k_{36} [C_6H_6CF_3^+] [A^-]$$

$$= \frac{k_{34} [CF_3^+] [C_6H_6]}{1 + \frac{k_{35}}{k_{36}} [A^-]}$$

As a first approximation, k_{33} , k_{34} , and k_{36} could be considered temperature independent, i.e., the activation energies for the formation of $C_6H_6CF_3^+$ ion-molecule intermediate. Both the radical abstraction reaction of $R^\bullet$ with $C_6H_6CF_3^\bullet$ and the dissociative neutralization reaction of $C_6H_6CF_3^+$ with a negatively charged species can be considered negligible. Positive activation energies, on the other hand, are expected for Reactions 31 and 32 and possibly Reaction 35. In the case of Reaction 31, this is based on the CF_3 affinity studies carried out by Szwarc and others. In the case of Reaction 32, a

positive energy of activation is postulated on the basis of the experimental observations of Majer, Phillips, and Robb (ref. 22) on the decomposition of the $C_6H_6CF_2Cl$ adduct. A positive energy of activation is also based on the consideration that Reactions 2 and 3 constitute forward and reverse reactions between $CF_3^\bullet$, C_6H_6 , and $C_6H_6CF_3$, which involve the same transition complex and which should thus exhibit temperature effects with activation energies related to each other on the basis of the energy levels of the respective initial reaction species. Similarly, the possibility of a temperature dependence on the dissociation of the $C_6H_6CF_3^+$ ionic intermediate in Reaction 6 is postulated as a parallel of the thermal-induced redissociation of the additional radical intermediate $C_6H_6CF_3^\bullet$.

By designating the Arrhenius activation energies for Reactions 31, 32, and 35 as E_{31} , E_{32} , and E_{35} ,

$$k_{31} = k_{31,0} \exp(-E_{31}/RT)$$

$$k_{32} = k_{32,0} \exp(-E_{32}/RT)$$

$$k_{35} = k_{35,0} \exp(-E_{35}/RT)$$

Then

$$\left(\frac{d[C_6H_5CF_3]}{dt} \right)_R = \frac{k_{31,0} [CF_3] [C_6H_6]}{1 + \frac{k_{31,0}}{k_{33} [R^\bullet]} \exp(-E_{32}/RT)}$$

and

$$\left(\frac{d[C_6H_5CF_3]}{dt} \right)_I = \frac{k_{34} [CF_3^+] [C_6H_6]}{1 + \frac{k_{35,0}}{k_{36} [A^-]} \exp(-E_{35}/RT)}$$

Although a rigorous analysis of the above equations requires solutions of the values of the intermediates $[CF_3]$, $[CF_3^+]$, $[R\cdot]$, and $[A^-]$ and cannot be justified by the extent of the available experimental data, an approximate analysis could nevertheless be made on the following basis. Because of the relatively small variations in the $G(C_6H_5CF_3)$ value (within a factor of two), the concentrations of the intermediates probably also vary only slowly. Thus they can be considered almost relatively constant, if much larger and physically meaningful temperature variations are indeed exhibited by the exponential terms in the preceding formula.

By assuming that the foregoing treatment constitutes a reasonable description of the experimentally observed radiolytic formation of $C_6H_5CF_3$, the experimental results can then also be resolved into two components: radical and ionic. Such a treatment is indicated graphically in Figure 3, in which the ionic component is taken to be essentially temperature independent over the range 27 to 180°C. On the other hand, the radical component becomes significant only at temperatures above 120°C, reaches a maximum value at approximately 200°C, and decreases with further increases in the irradiation temperature.

Figure 3. RESOLUTION OF $\text{C}_6\text{H}_5\text{CF}_3$ INTO RADICAL AND IONIC COMPONENTS

Analyzing first the radical component between 120 and 180°C, we obtain readily an activation energy corresponding to $E_{31} = 5.0$ kcal/mole, as shown in the Arrhenius plot in Figure 4. This value compares favorably with the values obtained by Holmes and Kutschke, 4.4 ± 0.4 (ref. 18), or Charles, 5.2 ± 0.4 (ref. 23), and thereby provides an indication of the probable validity of an analysis.

The magnitude of E_{32} , the energy of activation for the dissociation of the $[C_6H_5CF_3]^\cdot$ complex, can now be estimated on the basis of the value of E_{31} . If $[CF_3^\cdot][C_6H_6]$ can be considered approximately temperature independent, the relative increase of the term $k_{31}[CF_3^\cdot][C_6H_6]$ can be readily calculated as a function of temperature. On the other hand, since

$$\left(\frac{d[C_6H_5CF_3]}{dt} \right)_R = \frac{k_{31}[CF_3^\cdot][C_6H_6]}{1 + \frac{k_{32,0}}{k_{33}[R^\cdot]} \exp(-E_{32}/RT)}$$

a comparison of the calculated values of $k_{31}[CF_3^\cdot][C_6H_6]$, i.e., $k_{31,0}[CF_3^\cdot][C_6H_6] \exp(-E_{31}/RT)$, with the radical component of the experimental $C_6H_5CF_3$ yield will provide a direct measurement of $\frac{k_{32,0}}{k_{33}[R^\cdot]} \exp(-E_{32}/RT)$; specifically,

$$\frac{k_{31,0}[CF_3^\cdot][C_6H_6] \exp(-E_{31}/RT)}{\left(\frac{d[C_6H_5CF_3]}{dt} \right)_R} - 1 = \frac{k_{32,0}}{k_{33}[R^\cdot]} \exp(-E_{32}/RT)$$

Figure 4. ARRHENIUS PLOT OF THE RADICAL COMPONENT OF $\text{C}_6\text{H}_5\text{CF}_3$ FORMATION

and

$$\ln \left\{ \frac{k_{31,0} [\text{CF}_3] [\text{C}_6\text{H}_6] \exp(-E_{31}/RT)}{\left(\frac{d[\text{C}_6\text{H}_5\text{CF}_3]}{dt} \right)_R} - 1 \right\} = \ln \frac{k_{32,0}}{k_{33} R^\bullet} - \frac{E_{32}}{RT}$$

A plot of

$$\ln \left\{ \frac{k_{31,0} [\text{CF}_3] [\text{C}_6\text{H}_6] \exp(-E_{31}/RT)}{\left(\frac{d[\text{C}_6\text{H}_5\text{CF}_3]}{dt} \right)_R} - 1 \right\}$$

as a function of $1/T$ (Figure 5) shows that $E_{32} = \text{kcal/mole}$ and

$$\frac{k_{3,0}}{k_4 [R^\bullet]} = 3.7 \times 10^6.$$

Comparison of the values of E_{32} , the activation energy for the decomposition of $\text{C}_6\text{H}_6\text{CF}_3^\bullet$ radical addition product, with E_{31} , the activation energy for its formation, shows that E_{32} is larger than E_{31} by some 9 kcal/mole. Our value of E_{32} also compares with the value of 11.4 ± 0.8 kcal/mole determined by Majer, Phillips, and Robb (ref. 22) for the decomposition of the $\text{C}_6\text{H}_6\text{CF}_3^\bullet$ adduct, and thus lend support to the belief that the proposed mechanism represents a reasonable description of the $\text{CF}_3^\bullet + \text{C}_6\text{H}_6$ system, i.e.,

Figure 5. ARRHENIUS PLOT FOR THE DISSOCIATION OF $[C_6H_6CF_3]$.

Furthermore,

This value appears to be reasonable in view of the known ease of the radical addition reaction.

Although E_{35} , the activation energy for the redissociation of the ion-molecule intermediate, $\text{C}_6\text{H}_6\text{CF}_3^+$, can also be evaluated in a similar manner, this has not been carried out. Such an effort could not be justified on the basis of the available high-temperature experimental data.

As shown by the $\text{C}_6\text{H}_5\text{F}$ data plotted in Figure 6, the overall Arrhenius activation energy for the formation of $\text{C}_6\text{H}_5\text{F}$ is 2.1 kcal/mole, which is considerably lower than the value for the $\text{C}_6\text{H}_5\text{CF}_3$ system. Both this magnitude of the overall activation energy and the monotonical nature of the temperature effect afford evidence that the observed formation of $\text{C}_6\text{H}_5\text{F}$ is due to the rate-determining radical process, which involves atomic F and a C_6H_6 molecule, and is followed by a fast radical-radical hydrogen abstraction reaction:

The lower activation energy for the formation of the $\text{C}_6\text{H}_6\text{F}\cdot$ radical addition intermediate, as compared with that for $\text{C}_6\text{H}_6\text{CF}_3\cdot$, is entirely reasonable because of both the greater reactivity and the smaller steric hindrance in the case of the F atom. Consequently, a more favorable energy balance and a lower energy of activation can be expected in the reaction path of the $\text{F} + \text{C}_6\text{H}_6$ system.

Figure 6. ARRHENIUS PLOT FOR C_6H_5F FORMATION

On the basis of mass spectrometric data, the 100-eV yield of CF_2Br^+ ions and consequently that of the complementary F atoms from the ionic process should be on the order of 0.6 to 0.7. Since a comparable yield of F atoms formed through the homolytic dissociation of CF_3Br can also be expected, the overall yield of F atoms would be ~1.2 to 2. This value compares satisfactorily with the yield of $\text{C}_6\text{H}_5\text{F}$ at high temperatures when all, or at least most, of the F atoms were utilized in the formation of $\text{C}_6\text{H}_5\text{F}$.

4.2. Preparative Experiments

Limited work was carried out to produce radiation-synthesized fluoroaromatics on a preparative scale. After a positive feasibility had been demonstrated, this effort was terminated since more benefit would be obtained through a better understanding of the nature of the radiation fluorination process and the radiation chemistry of F_2 compounds.

4.2.1. Experimental

4.2.1.1. Sample Preparation and Irradiation

In order to produce a relatively large quantity of product, a 12.44-liter vessel was fabricated from stainless steel. It was designed with a removable top for easy access to the interior. The cover has three wells, which are welded vacuum tight and which allow the sources to be lowered into the vessel, thus maximizing the use of radiation.

The vessel was filled with appropriate samples and irradiated with about 3400 curies of cobalt 60 for 261 hours. The vessel was heated with heating tapes to keep the sample in the vapor phase.

4.2.1.2. Product Analysis

The sample for this experiment was collected by immersing a metal vessel made from 1/2-in. stainless tubing in liquid nitrogen. The reaction vessel was heated with heating tapes to drive the volatile vapors out of the tar-like polymers. After 36 hours in the liquid nitrogen, the 1/2-in. vessel was transferred to the vacuum line to separate the gaseous products (at ambient temperature) from the liquid products.

4.2.2. Results

Several experiments were carried out and the products analyzed. As a rule, the products were qualitatively similar to those found in the laboratory-scale experiments. However, the products were not quantitatively reproducible, and a rather long experimental time was required for each experiment. Consequently, these efforts were terminated in favor of the process mechanism studies.

4.3. Fluorobenzene-Sensitized Dimerization of Toluene

In an effort to evaluate the relative effectiveness of various F_2 compounds in the gas-phase fluorination of aromatics and in the presence of cobalt 60 gamma rays, a study was initiated by using CF_4 , SiF_4 , BF_3 , and SF_6 and $CH_3C_6H_5$ as the aromatic substrate. Fluorination had been observed directly only in the

$\text{CF}_4\text{-CH}_3\text{C}_6\text{H}_5$ system. However, the radiolysis of $\text{CH}_3\text{C}_6\text{H}_5$ vapor was markedly enhanced by all these compounds. In order to better understand this sensitization, a more detailed study of the $\text{SF}_6\text{-CH}_3\text{C}_6\text{H}_5$ system was carried out. SF_6 was chosen because it is the most effective sensitizer of the compounds tested.

4.3.1. Experimental

4.3.1.1. Materials and Sample Preparation

The $\text{CH}_3\text{C}_6\text{H}_5$ used was analytical reagent grade and was dried with anhydrous sodium sulfate prior to use. Sulfur hexafluoride was obtained from the Matheson Company with a listed purity of 98.0 mole percent and was purified by sublimation on a vacuum line. Iodine was a Merck-resublimed product and was used without further purification.

The samples were prepared by degassing a weighed amount of $\text{CH}_3\text{C}_6\text{H}_5$ in the sample vessel and distilling the required amount of SF_6 into the vessel. The vessel was then sealed off, and the contents were maintained at liquid nitrogen temperature. The total pressure of the samples varied from 600 mm Hg to 3 atm. Most samples had pressure of 1 to 3 atm. The size of the sample vessel was approximately 200 cc.

4.3.1.2. Sample Irradiation

Irradiations were carried out in an air bath consisting of a Glas-Col-M-636 heating mantle fitted with a top plate that supported the source holder and sample vessel holders. Temperature was maintained at $105 \pm 5^\circ\text{C}$ by using a Fenwall Thermoswitch thermoregulator. The radiation dose rate was 1×10^{18} ev/gram-hour.

4.3.1.3. Product Analysis

Gaseous radiolysis products were not determined. Liquid products were analyzed by gas chromatography. A 30-ft column containing 30 wt. % Apiezon L on crushed firebrick was used as the packing. Analyses were performed on an F and M model 202-B linear temperature programmed gas chromatograph. The temperature was varied from 125 to 253°C at a heating rate of 2.3°/min. Identifications were made by comparing retention times of known compounds with those of irradiated samples. The chromatographic areas were determined with a hand planimeter, which was reproducible to 0.1 cm² (approximately 0.02 micromoles).

4.3.2. Results

The results of the vapor-phase radiolysis of $\text{CH}_3\text{C}_6\text{H}_5$ in the presence of various amounts of SF_6 are given in Table 12 and Figure 7.

Observations on the gas-phase radiolysis of $\text{CH}_3\text{C}_6\text{H}_5\text{-SF}_6$ systems were as follows:

- (1) Direct fluorination was not observed.
- (2) There were qualitative indications of aromatic- SF_6 compounds being formed. The relative G values were small, i.e., $\lesssim 0.4$.
- (3) The hydrocarbon products were biphenyl, bibenzyl, and bitolyls; the bitolyls were the major product. The m,m' and p,p' isomers were tentatively identified.

Table 12

RESULTS OF VAPOR-PHASE RADIOLYSIS OF TOLUENE IN THE PRESENCE OF SF₆^a

X_F	Initial Toluene, mmoles	Initial SF ₆ , mmoles	G Values ^b		
			Biphenyl	Bibenzyl	Bitolyls ^c
0	2.80		-	-	3.07 0.37
.160	3.72	0.52	-	-	4.86 0.70
.342	3.82	1.42	-	-	6.10 0.69
.370	3.68	1.54	-	-	5.90 0.67
.506	3.83	2.81	-	0.15	5.88 1.0
.584	2.67	3.71	0.10	0.33	4.47
.689	3.88	6.11	0.09	0.15	8.54 1.2
.735	3.57	7.06	0.16	0.19	8.85 1.3
.763	3.01	6.88	0.19	0.47	9.95
0.934	1.23	12.1	0.10	0.24	7.00

^aAll irradiations were carried out at $105 \pm 5^\circ\text{C}$ in the dark for a period of 120 hours.

^bG values were calculated by using the approximate dose rate of 10^{18} eV/gram-hour. The number of moles of product was calculated from the chromatographic area fraction (relative to toluene) multiplied by the initial moles of toluene. Equal chromatographic calibration coefficients were assumed. The latter assumption invalidates the use of the data for absolute G values, but for the C₁₄ compounds of interest, internal consistency is obtained since the calibration coefficients are equal, within experimental error, for the isomers. Where a value is absent, the product could not be measured.

^cThe two columns refer to two products that were not completely resolvable under the conditions of analysis.

Figure 7. RADIOLYSIS OF TOLUENE-SULFUR HEXAFLUORIDE MIXTURES

- (4) The G values of these products increased linearly with increasing electron fractions of SF_6 (X_F) up to $X_F = 0.75$; a point taken at $X_F = 0.93$ indicated a threefold increase, which was also observed in the yield of fluorinated product from the $\text{CF}_4\text{-CH}_3\text{C}_6\text{H}_5$ system.

There is a distinct possibility that some of the products tentatively identified as bitolyls are benzyltoluenes; consequently these products are listed as C_{14} compounds. The relative amounts of these C_{14} compounds remain constant under the conditions of our experiment; furthermore both $G(\text{bibenzyl})$ and $G(\text{bitolyl})$ have the same qualitative dependence on X_F . These results suggest the same mechanism for their production.

4.3.3. Process Mechanism Considerations

In the radiolysis of vapor-phase $\text{CH}_3\text{C}_6\text{H}_5$ a smaller number of products was observed, as compared with the liquid-phase radiolysis of C_6H_6 . However, the conditions used in the latter study promoted the formation of products to a measurable size. Undoubtedly, the larger effective mean free path of the energetic aromatic species in the gas phase allows for a less complex chemistry to be obtained.

The G values for biphenyl are consistently lower than those for bibenzyl. If it is assumed that benzyl radicals are formed from $\text{CH}_3\text{C}_6\text{H}_5$ by hydrogen abstraction by methyl radicals that result from the dissociation of $\text{CH}_3\text{C}_6\text{H}_5$, a 1:1 correspondence between biphenyl and bibenzyl would be expected. This

correspondence also assumes that phenyl and benzyl radicals both reacted to form their respective dimers or their cross product (diphenylmethane). Since this correspondence is not obtained, the phenyl radical must have a more efficient path of dimerization for reaction than the benzyl radical. The phenyl radical can add efficiently to aromatics, whereas the benzyl radical (a substituted methyl radical) will probably react by hydrogen abstraction from, predominantly, the methyl group of $\text{CH}_3\text{C}_6\text{H}_5$. The latter reaction will merely produce another benzyl radical and thus allow a higher probability for a benzyl-benzyl encounter.

5. CONCLUSIONS

5.1. Radiation Chemistry of Simple Fluorocarbons

(1) Despite the well-established thermal and chemical stability of the C-F bond, the radiation stability of fluorocarbons is comparable with, though somewhat higher than, that of the hydrocarbons.

(2) In common with other chemical systems, both ionic and radical intermediates can be produced when radiation interacts with a fluorocarbon. The C-F bond of such compounds is, however, inert toward the radical intermediates, although it can be attacked by at least one F_2 -containing ion, i.e., CF_3^+ , to undergo a F atom abstraction reaction.

(3) The primary G values of the intermediates are on the order of 2 to 3 or less. As an approximation, the ionic intermediates appear to have distributions comparable with those found by mass spectrometric investigation.

(4) The abstraction of a F atom by CF_3^+ is believed to involve a small, but finite, energy of action, which is estimated to be ~ 0.4 kcal/mole.

5.2. Radiation Synthesis of Fluorinated Aromatics

(1) Our previous observation that radiation-induced fluorination of aromatic compounds will lead to the formation of products retaining the aromatic character has been further confirmed by this research. However, since the G values of the products are on the order of 2 to 3 or less, this method appears to be practical only for special applications. The high commercial value of F_2 compounds, however, might permit modification of this conclusion.

(2) Both radical and ionic processes could result in the observed aromatic fluorination process.

(3) The radiation-induced fluorination process exhibits a temperature effect; i.e., the radical processes are more sensitively affected. This effect would permit the preferential introduction of predetermined fluorine-containing groups into aromatic molecules.

(4) The definite contribution of a relatively temperature-independent ionic mechanism to the radiation-induced fluorination process, coupled with the known existence of ionic species such as CF_2Cl^+ , CF_2Br^+ , CF_2I^+ , etc., suggests the use of this method for the preparation of heat-sensitive F_2 compounds either as end products or as reactive intermediates. Consequently, this method could be particularly useful in the synthesis of biologically or physiologically active compounds.

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