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GAS PHASE RADIATION CHEMISTRY OF HEXAFLUOROETHANE

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SUMMARY

The Co-60 gamma radiolysis of gaseous C_2F_6 was investigated at 50 Torr pressure, both pure and with 10% oxygen added. For the pure system, the radiolytic products and their respective G values were CF_4, 2.27; C_3F_8, 0.23; C_4F_{10}, 0.09; C_5F_{12}, 0.015; and C_6F_{14}, 0.009. All radiolysis products except for CF_4 (G = 0.61) were eliminated when 10% O_2 was added as scavenger. The results are discussed mainly in terms of the decomposition of excited C_2F_6 into free radicals, which can then combine. The unscavenged CF_4 is accounted for by the ion-molecule reaction $CF_3^+ + C_2F_6 \longrightarrow CF_4 + C_2F_5^+$.

INTRODUCTION

The gas phase radiolysis of hexafluoroethane has been investigated previously in the laboratories of Kevan [1,2] and Cooper [3]. These reports include yields from the pure system as well as the effect of either 1% O_2 [1,2], or 1-20% Br_2, Cl_2 or HCl [3] added as scavengers. Radiolysis of liquid C_2F_6 [2] as well as the effect of rare gas sensitization in both the gas [4] and liquid [5] phases have also been reported.

We recently found it necessary to reinvestigate the radiolysis of pure C_2F_6 to establish an 'end-point' for an investigation of the radiolysis of C_2F_6 - C_2H_6 gas phase mixtures [6]. Yields found for the major products CF_4, C_3F_8, and C_4F_{10} are in reasonable agreement with the earlier work. New results include yield measurements for the minor products C_5F_{12} and C_6F_{14}, as well as determination of the effect of a 10-fold higher concentration of O_2 scavenger on the system. The Discussion section includes relevant ion-molecule reaction data on the system [7-11] which was not available when the earlier work appeared.

EXPERIMENTAL

Hexafluoroethane obtained from PCR, Inc. was purified by preparative gas chromatography and transferred into 104 cc nickel radiolysis vessels by standard vacuum line techniques. Analysis of radiolysis products and products from the ethylene dosimeter was carried out on a special dual column, dual detector gas chromatograph with a Toepler pump input section [12]. Irradiations were performed using a 'Wisconsin-Type' Co-60 gamma irradiator which has been described previously [13]. The dose rate in 50 Torr ethylene ($G(H_2) = 1.2$) [14] was 3.15×10^{19} eV/g hr. After correcting for the difference in secondary electron stopping power, the dose rate in 50 Torr hexafluoroethane was calculated as 2.46×10^{19} eV/g hr. Further details on sample preparation and analysis methods are given elsewhere [6].

RESULTS

Hexafluoroethane was irradiated at room temperature over the absorbed dose range of 0.738×10^{20} to 9.84×10^{20} eV/gram. Most radiolyses were carried out at 50 Torr; however, experiments at pressures of 20 and 100 Torr were also performed. The product G values were independent of pressure over this range. The three major products are tetrafluoromethane, octafluoropropane, and decafluorobutane, and two minor products are perfluoropentane and perfluorohexane. No unsaturated fluorocarbon compounds were found. The major products and the minor product C_6F_{14} were identified by their retention times and their mass spectral cracking patterns. C_5F_{12} was only identified by mass spectrometry. Figures 1 and 2 show that the yields of the major products are proportional to absorbed dose. Yields of all products are listed in Table 1, along with results of earlier investigations.

Table 1 also shows the effect of adding oxygen to the hexafluoroethane prior to radiolysis. The G value for tetrafluoromethane was reduced by approximately 75%, while the other radiolysis products were eliminated completely.

DISCUSSION

Table 1 compares the results of this work with that of Cooper and Haysom [3] and also Kevan and co-workers [1,2]. In the pure system there seems to be reasonable agreement in the yields of the major products.

TABLE 1.

Radiolysis yields for hexafluoroethane

Product	G Values[a]							
	Kevan[b]		Cooper[c]				This work	
	Pure	1% O_2	Pure	5% Br_2	5% Cl_2	5% HCl	Pure	10% O_2
CF_4	2.45	1.3	2.50	0	0.40	0.26	2.27	0.61
C_3F_8	0.40	0	0.31	0	0	0	0.23	0
C_4F_{10}	0.15	0	0.10	0	0	0	0.09	0
C_5F_{12}	—	0	—	0	0	0	0.015	0
C_6F_{14}	—	0	—	0	0	0	0.009	0

[a] G value is defined as molecules consumed or produced per 100 eV energy absorbed.

[b] L. Kevan and co-workers, Reference 1 and 2.

[c] R. Cooper and H. R. Haysom, Reference 3. Yields of H-, Cl-, and Br- containing products of the scavenging reactions are also reported.

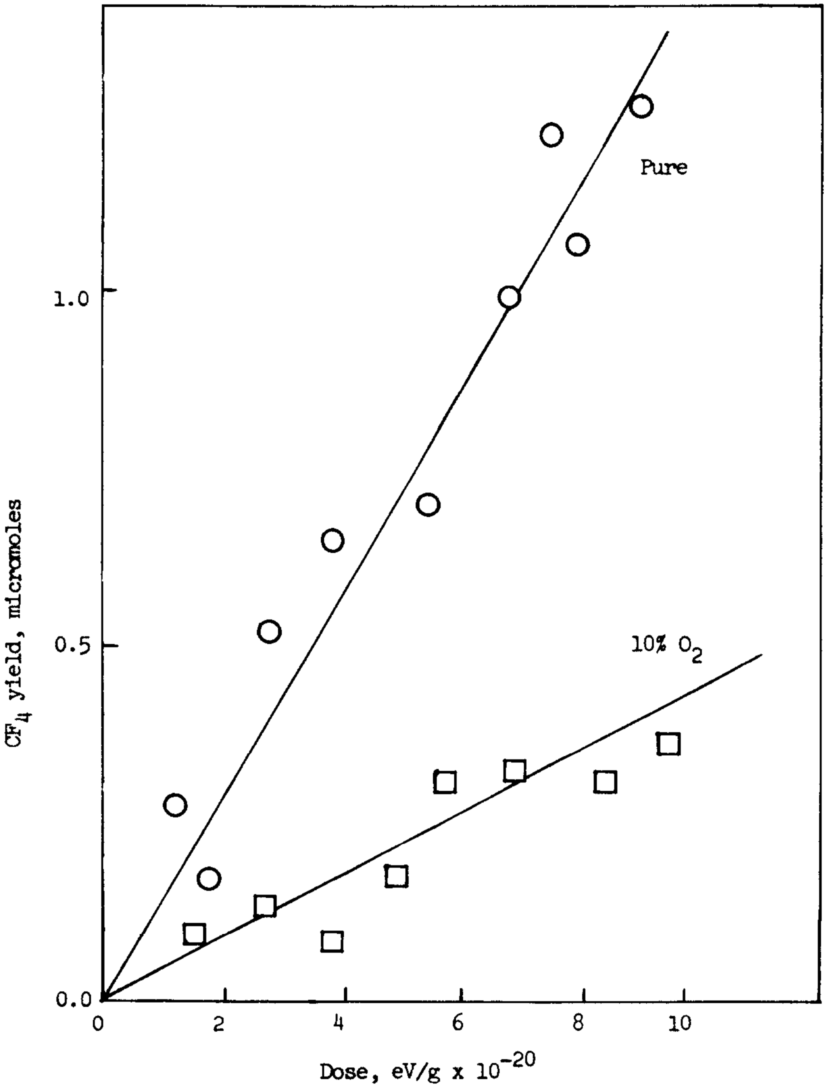

Fig. 1 Production of CF_4 (pure, ○ ; 10% O_2, □) as a function of dose.

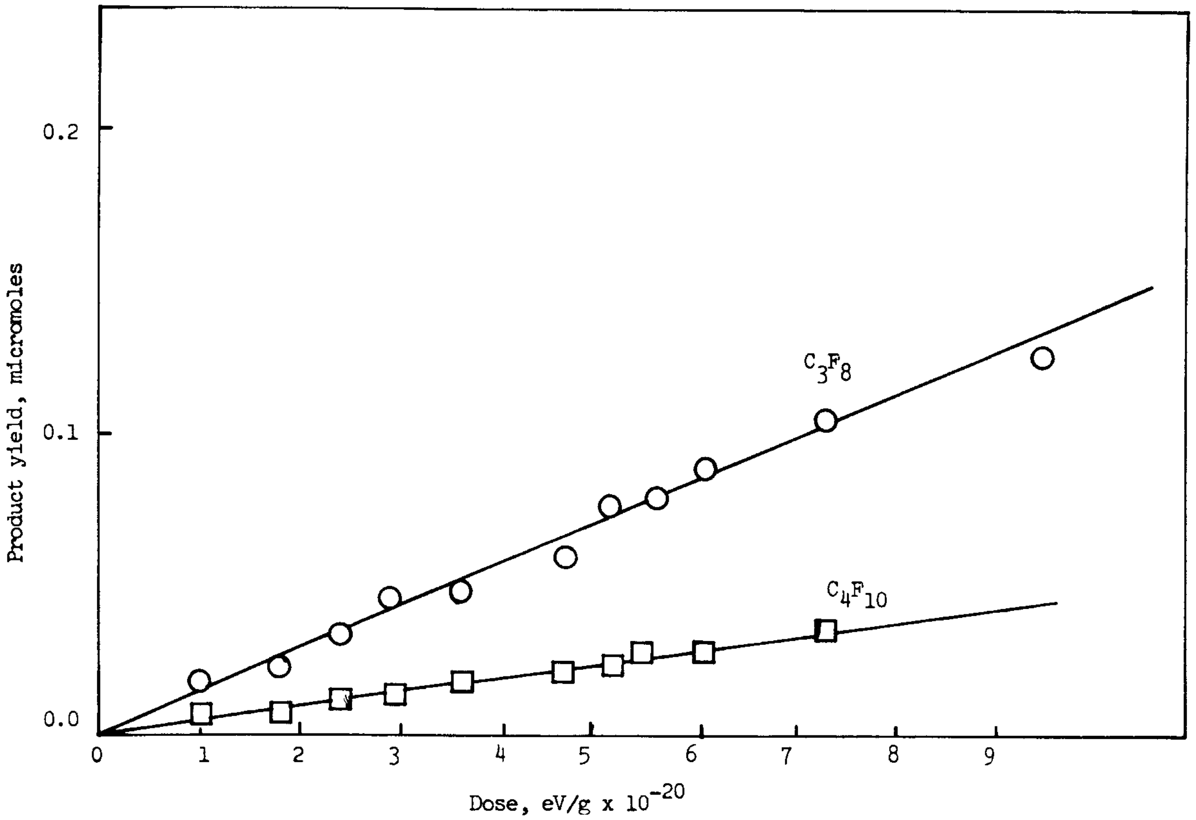

Fig. 2 Production of C_3F_8 (pure, ○) and C_4F_{10} (pure, ▣) as a function of dose.

Kevan's laboratory reported the formation of C_5F_{12} and C_6F_{14}, but did not give any yield data on them [1,2]. Cooper and Haysom reported seeing higher molecular weight products, but were not able to identify these products with certainty [3]. In all three studies, the material balance is not particularly good with a fluorine to carbon ratio of 3.35 to 1 for the results of Kevan and co-workers [1,2], 3.52 to 1 for Cooper and Haysom's results [3], and 3.56 to 1 for this work.

It was found in all three studies that when a radical scavenger is added to C_2F_6, all higher molecular weight products disappear. Some differences are apparent, however, in the effect of the various scavengers on the yield of tetrafluoromethane. Cooper and Haysom [3] investigated residual yields of CF_4, as well as yields of various products of the scavenging reactions, at concentrations of added Br_2, Cl_2, and HCl in the range of 0.5 to 20 mole/percent Most yields tended towards plateau values, becoming constant after ca. 3 to 5% scavenger was added. (These were minor exceptions in the case of added HCl: the CF_3H yield tended to decrease slightly when more than 5% HCl was added, whereas a plateau in the C_2F_5H yield was reached only upon addition of ca. 10% HCl.) Cooper and Haysom found plateau yields for tetrafluoromethane of 0.40 with added chlorine and 0.26 with added HCl. Addition of Br_2 to the plateau region (ca. 3%) left no residual yield of tetrafluoromethane. Kevan et al [1,2] found a residual CF_4 yield of 1.3 when 1% oxygen was added to C_2F_6. This yield may be less than the plateau value, however, in view of the results of Cooper and Haysom [3] showing that typically 3 to 5% scavenger was required to reach the plateau. Utilizing 10% added oxygen, which is well into the plateau region for all scavengers studied by Cooper and Haysom, we find a residual CF_4 yield of 0.61. The nature of the residual CF_4 yield, which remains unscavenged in the presence of several percent added HCl, Cl_2, or O_2, will be discussed later in this section.

Although the results of scavenger studies in this and other laboratories [1-3] clearly support a free radical mechanism for ultimate formation of all products except the residual portion of the CF_4 yield, the primary effects of high energy radiation on C_2F_6 must involve both excitation and ionization processes.

$$C_2F_6 \rightsquigarrow C_2F_6^+ + e^- \qquad (1)$$

$$\rightsquigarrow C_2F_6^* \qquad (2)$$

$$C_2F_6^* \longrightarrow 2CF_3\cdot \qquad (3)$$

$$\longrightarrow CF_4 + CF_2 \qquad (4)$$

$$C_2F_6^* \longrightarrow C_2F_5\cdot + F\cdot \qquad (5)$$

$$C_2F_6^{+} \longrightarrow CF_3^{+} + CF_3\cdot \tag{6}$$

$$\longrightarrow C_2F_5^{+} + F\cdot \tag{7}$$

$$CF_3^{+} + e^{-} \longrightarrow (CF_3\cdot{*}) \longrightarrow CF_2 + F\cdot \tag{8}$$

$$\xrightarrow{(m)} CF_3\cdot \tag{9}$$

$$C_2F_5^{+} + e^{-} \longrightarrow (C_2F_5\cdot{*}) \longrightarrow CF_3\cdot + CF_2 \tag{10}$$

$$\searrow\!\!\longrightarrow C_2F_4 + F\cdot \tag{11}$$

$$\xrightarrow{(m)} C_2F_5\cdot \tag{12}$$

Neutral fragmentation processes (3-5), originally suggested by Kevan and Hamlet [1], are consistent with the observed products in the unscavenged system as well as with the halogen containing products of Cl_2 and Br_2 scavenging studies, done by Cooper and Haysom [3]. Ionic fragmentation processes (6) and (7) are supported by the fact that CF_3^{+} ion (58% of the total ion intensity) and $C_2F_5^{+}$ (24%) are the major observed ions in the mass spectrometric fragmentation of C_2F_6 [25]. Smaller amounts of CF^{+} (11%) and CF_2^{+} (5%) are also seen, so that some further fragmentation of initially formed ions must also occur.

Since rupture of the C-F bond requires about 25 kcal/mole more energy than rupture of the C-C bond, fragmentation of $C_2F_6{*}$ into $C_2F_5\cdot + F$ should be considerably less important than formation of $2CF_3\cdot$ or $CF_4 + CF_2$, both of which involve breaking the weaker C-C bond. Bromine and chlorine scavenger results of Cooper and Haysom show yield ratios (½G for C_1 products)/(G for C_2 products) of 0.45 and 1.04 respectively. However, the thermodynamic expectation is clearly obeyed if allowance is made for the fact that the parent compound has 6 C-F bonds and only 1 C-C bond; inherent bond rupture probability for C-C versus C-F is in the range of 3:1 (bromine results) to 6:1 (chlorine results).

Sokolowska and Kevan [2] postulated a series of radical combination reactions leading to F_2, CF_4, C_3F_8, and C_4F_{10} formation in the C_2F_6 radiolysis system:

$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6 \tag{13}$$

$$CF_3\cdot + C_2F_5\cdot \longrightarrow C_3F_8 \tag{14}$$

$$C_2F_5\cdot + C_2F_5\cdot \longrightarrow C_4F_{10} \tag{15}$$

$$F\cdot + F\cdot + M \longrightarrow F_2 + M \tag{16}$$

$$CF_3\cdot + F\cdot \text{ (or } F_2) \longrightarrow CF_4 \text{ } (+F\cdot) \tag{17}$$

$$C_2F_5\cdot + F \text{ (or } F_2) \longrightarrow C_2F_6 \text{ } (+F\cdot) \tag{18}$$

Fluorine is probably completely consumed by reaction with perfluoroalkyl radicals, or with the walls. Back-reactions (13) and (18) must occur in this system, but are not directly observable.

Evidence from photochemical studies indicates that unlike hydrocarbons, fluorocarbon radicals do not disproportionate [17-19] and fluorine atoms do not abstract fluorine from fluorocarbons [20-22]. Therefore, Reactions (13) through (18) are adequate to explain the experimental results; they all have zero or small activation energies [23,24].

Observation of C_5F_{12} and C_6F_{14} as scavengable products requires participation of $C_3F_7\cdot$ radicals in the reaction scheme. Addition of $CF_3\cdot$ to C_2F_4 would be one way to account for this intermediate. However, formation of olefinic products has not been observed during the radiolysis of any non-cyclic perfluoroalkane. An alternate plausible route is combination of $C_2F_5\cdot$ radicals to give an excited C_4F_{10} intermediate, which can either be deactivated by collision or re-fragment:

$$C_2F_5\cdot + C_2F_5\cdot \longrightarrow (C_4F_{10})^* \tag{19}$$

$$(C_4F_{10})^* + M \longrightarrow C_4F_{10} + M \tag{20}$$

$$(C_4F_{10})^* \longrightarrow C_2F_5\cdot + C_2F_5\cdot \tag{21}$$

$$(C_4F_{10})^* \longrightarrow CF_3\cdot + C_3F_7\cdot \tag{22}$$

The $C_3F_7\cdot$ radical could then dimerize to give C_6F_{14}, or react with $C_2F_5\cdot$ forming C_5F_{12}. Reaction with $F\cdot$, F_2, or $CF_3\cdot$ would also occur, forming small additional amounts of C_3F_8 and C_4F_{10}, respectively. An additional route to the $C_3F_7\cdot$ radical involves insertion of difluorocarbene, formed in Reaction (4), into substrate:

$$CF_2 + C_2F_6 \longrightarrow (C_3F_8{}^*) \tag{23}$$

$$C_3F_8{}^* \longrightarrow CF_3\cdot + C_2F_5\cdot \tag{24}$$

$$\longrightarrow C_3F_7\cdot + F\cdot \tag{25}$$

The arguments presented above concerning excited C_2F_6 apply to excited C_3F_8 as well, and Reaction (24) should be more important than Reaction (25). Even so, Reaction (25) could be a significant source of the small yield of $C_3F_7\cdot$ radical needed to account for the C_5 and C_6 products in this system.

Kevan and Hamlet [1] postulated that the unscavengable CF_4 was due either to molecular dissociation of C_2F_6 into CF_4 plus CF_2 (Reaction 4) or to one of the following ion-molecule reactions:

$$CF_3{}^+ + C_2F_6 \longrightarrow CF_4 + C_2F_5{}^+ \tag{26}$$

$$C_2F_5{}^+ + C_2F_6 \longrightarrow CF_4 + C_3F_7{}^+ \tag{27}$$

As mentioned above, CF_3^+ and $C_2F_5^+$ are the main ions in the mass spectrum of C_2F_6, so that reactions of either or both of these species could be important. Reaction (27) can be eliminated since the $C_3F_7^+$ ion has never been observed in the mass spectrometric investigations of C_2F_6 [7-11]. In fact, it has been shown that $C_2F_5^+$ ions produced either as primary fragments or as reaction products are essentially unreactive with C_2F_6 [7-11].

Although Reaction (26) is thought to be endothermic, Marcotte and Tiernan [8] observed it using a tandem mass spectrometer and suggested that this reaction occurred because in their experiments CF_3^+ had as much as 2.9 eV excess internal energy. More recently Ausloos and co-workers [10] investigated this reaction using a photoionization mass spectrometer, in which it was shown that CF_3^+ ions having no internal energy undergo Reaction (26), with a rate constant of 4×10^{-11} cm^3/molecule-second at pressures below 0.01 Torr. Although this reaction is slow, it appears that it is a major source of the unscavenged CF_4 when oxygen is used as a scavenger. Cooper and Haysom's results [3] which show only small amounts of CF_4 in the presence of chlorine and hydrogen chloride, and no CF_4 in the presence of bromine, seem to imply that there is some type of ionic process involved when these scavengers are present which would interfere with Reaction (26). They suggest this possibility particularly when HCl is the scavenger. Amphlett and Whittle [26] report that photochemically generated $CF_3\cdot$ radicals react with HCl to give CF_3H exclusively, whereas Cooper and Haysom [3] found that when C_2F_6 was irradiated in the presence of 5% HCl, not only CF_3H (G = 1.6), but also CF_3Cl (G = 1.0) was formed. Since Reaction (23) is fairly slow, it probably could be suppressed in the presence of reactive additives which remove CF_3^+.

Reaction (4) is still a possibility, but Cooper and Haysom's results [3] with added bromine seem to cast doubt on it, as there is no reason to believe that small amounts of bromine would interefere with the primary decomposition of excited C_2F_6.

As mentioned above, all three of the investigations represented in Table 1 suffer from a material balance problem. Based on our own results we can write the stoichiometric relationship:

$$2.27\ C_2F_6 \longrightarrow 2.27\ CF_4 + 2.27\ CF_2 \qquad (28)$$

Even if all the 'surplus' CF_2 is assumed to contribute towards the measured yields of C_3F_8, C_4F_{10}, C_5F_{12}, and C_6F_{14}, there is still a shortage of CF_2 units with G = 1.78. Similar comments apply to the work of Cooper and Haysom [3] and Kevan and co-workers [1,2]. Comparison of our results with the earlier studies suggests that extended analytical efforts might reveal trace amounts of somewhat higher molecular weight products, but not in amounts sufficient to solve the material balance problem. It appears most reasonable to suggest formation of $(CF_2)_n$ polymeric deposits on the vessel walls.

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