TABLE IV

AVERAGE RATE CONSTANTS FOR ION-MOLECULE REACTIONS AT E = 12.5 VOLT/CM.

Reactions	k (cc./mol. sec.)
$Ar^+ + CH_4 \longrightarrow ArH^+ + CH_3$	0.20×10^{-10}
$Ar^+ + CH_4 \longrightarrow ArCH_2^+ + H_2$	$.008 \times 10^{-10}$
$Ar^+ + CH_4 \longrightarrow ArCH_3^+ + H$	$.003 \times 10^{-10}$
$Kr^+ + CH_4 \longrightarrow KrH^+ + CH_3$	$.122 \times 10^{-10}$
$Kr^+ + CH_4 \longrightarrow KrCH_2^+ + H_2$	$.010 \times 10^{-10}$
$Kr^+ + CH_4 \longrightarrow KrCH_3^+ + H$	$.030 \times 10^{-10}$
${}^aXe^+ + CH_4 \longrightarrow XeH^+ + CH_3$	$.38 \times 10^{-10}$
$Xe^+ + CH_4 \longrightarrow XeCH_2^+ + H_2$	$.0045 \times 10^{-10}$
$Xe^+ + CH_4 \longrightarrow XeCH_3^+ + H$	$.022 \times 10^{-10}$

[a] Taken from ref. 1.

average of 14 readings at different rare gas pressures. Agreements among replicate results were easily within a factor of 2. Previously obtained xenon–methane ion–molecule reaction rate constants are included in Table IV for comparative purposes.

TABLE V

AVERAGE RATE CONSTANTS FOR CHARGE EXCHANGE REACTIONS AT E = 12.5 VOLT/CM.

Reaction	k (cc./mole sec.)
$Ar^+ + CH_4 \longrightarrow Ar + H_2 + CH_2^+$	2.3×10^{-10}
$Ar^+ + CH_4 \longrightarrow Ar + H + CH_3^+$	9.1×10^{-10}
$Kr^+ + CH_4 \longrightarrow Kr + H + CH_3^+$	4.9×10^{-10}
$Kr^+ + CH_4 \longrightarrow Kr + CH_4^+$	7.4×10^{-10}

Rate constants for the ion–molecule reactions forming RH^+ and RCH_2^+, where R represents a rare gas atom, do not vary significantly with rare gas species, but the rate constant for the formation of $ArCH_3^+$ is an order of magnitude smaller than those for the formation of $KrCH_3^+$ and $XeCH_3^+$. Our values of 2.3×10^{-10} and 9.1×10^{-10} cc./mole sec. for rate constants for the formation of CH_2^+ and CH_3^+, respectively, by charge exchange in argon–methane mixtures compare with the values obtained by Melton of 3×10^{-10} and 16×10^{-10}.

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Preparation, Trapping, Identification and Chemistry of Captive Perfluoroalkyl Radicals. I

BY S. V. R. MASTRANGELO

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Perfluoroalkyl radicals were produced by passage of a radio frequency discharge through C_2F_6 and C–C_4F_8 gas and were trapped on a liquid nitrogen finger. They were identified by chlorination and bromination of the deposits followed by analysis of the products with gas chromatographic and mass spectrometric techniques. Warm-up products of the captive radicals and reaction products with tetrafluoroethylene also were identified. Identification of the products of reaction of the captive radicals with Cl_2, Br_2 and TFE, as well as with themselves on warming, showed that the radicals present in the blue deposit were CF_2: while those in the red deposit were CF_3.

Introduction

The stabilization of free radicals by trapping them at low temperatures[1] provides the opportunity to study at leisure the chemistry and physics of these normally transient and highly reactive intermediates. Several recent articles[2-4] present excellent reviews of this rapidly growing field. Progress in the study of the chemistry of these species also has been made in recent years. For example, Milligan and Pimentel[5] reported that the CH_2 radical produced by photolysis of diazomethane in solid argon and nitrogen at 20°K. reacts at 35°K. to form methane, ethylene, propylene, cyclopropane and polyethylene. A more complete survey of low temperature chemistry is given by Ralph Klein.[6]

In the present publication, a report is given of the method of preparation, trapping and identification of captive CF_2: and $CF_3\cdot$ radicals. Some physical and chemical properties of the trapped species are described. Included are halogen and fluoroölefin addition and radical transformation reactions which are accompanied by striking color changes.

Apparatus and Procedure

I. Apparatus.—The apparatus used for production of fluorocarbon radicals is shown schematically in Fig. 1. Gas from the cylinder marked "parent" was bled from two Hoke needle valves through a 3-inch diameter coil of $^1/_8$-inch copper tubing (to restrict the flow) preceded by a Maxisafe vacuum gauge. The rate of flow was calibrated against the pressure reading on this gauge. The pressures downstream from the copper coil were read on a McLeod gauge. These ranged from 0.1 to several mm.

The radical trap was 160 mm. in length from the top of the 45/50 standard joint and had an outside diameter of 55 mm. The cold finger o.d. was 25 mm. On some occasions, a rectangular finger was used for obtaining visible spectra. The use of vertical inlet and outlet tubes with stopcocks

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(1) See, for example, F. O. Rice and M. Freamo, *J. Am. Chem. Soc.*, **73**, 5529 (1951); **75**, 548 (1953); F. O. Rice and C. J. Grelecki, *ibid.*, **79**, 1880; 2679 (1957); *J. Phys. Chem.*, **61**, 824, 830 (1957).

(2) H. P. Broida, *Ann. N. Y. Acad. Sci.*, **67**, 530 (1957).

(3) H. P. Broida, "Endeavour," XVII, No. 68, 208 (1958).

(4) Arnold M. Bass and H. P. Broida, "Formation and Trapping of Free Radicals," Academic Press, Inc., New York, N. Y., 1960.

(5) D. E. Milligan and G. C. Pimentel, *J. Chem. Phys.*, **29**, 1405 (1955).

(6) Arnold M. Bass and H. P. Broida, "Stabilization of Free Radicals at Low Temperatures," U. S. Department of Commerce, N.B.S. Monograph 12 (1960).

allowed for positioning the trap in a Model 14 Cary Spectrophotometer.

The radical trap was provided with a grounded wire which entered through a Kovar-to-Pyrex seal. The wire intersected the axis of the feed tube near where it opened into the wall of the trap. The wire concentrated the discharge of an air-core Tesla coil (vacuum leak detector) applied to the surface of the trap near the grounded electrode. The discharge was thus concentrated in the region immediately upstream from the cold finger. Without the ground wire, the glow discharge was dissipated throughout the entire vacuum line, and the radical yield was reduced.

II. General Procedure.—The apparatus was first pumped down to 10^{-5} to 10^{-6} mm. by means of a mercury diffusion pump and warmed, where possible, with a hot-air blower to remove adsorbed water. The cold finger was then filled with liquid nitrogen and the inner electrode connected to a good ground (water or gas line). On humid days, the lower part of the apparatus was enclosed in a transparent cylindrical shell of "Lucite" and warm, dry nitrogen swept over the external surface of the radical trap (not shown in Fig. 1). This improved the radical yield. When present, moisture apparently conducted the surface charge away from the point of contact of the Tesla coil and changed a characteristic important in coupling the radio frequency to the grounded electrode (capacitive effect).

After filling the cold finger and grounding the inner electrode, an air-core Tesla coil was applied to the outer wall of the radical trap at several points near where the feed line enters the trap, while gas from the "parent" cylinder was fed in. The values on the "parent" cylinder (C_2F_6 or $C\text{–}C_4F_8$) were cracked and gas was fed into the trap at the rate of 10–20 g./hr. About 15 minutes was normally required to obtain appreciable quantities of radicals as indicated by the coloration. Longer generation times caused color changes due to radical transformations as will be discussed later.

In the warm-up experiments, the liquid nitrogen was removed by suction from the cold finger and the deposit, consisting of captive radicals embedded in a matrix of the frozen parent compound, was allowed to warm slowly by radiation through the vacuum space (5–10 min.). The stopcock to the main vacuum pump was closed during the warm-up and sampling period. As the solid deposit melted, the cold liquid fell to the bottom of the trap and evaporated. The vapors were sampled by admitting them to evacuated 100–500 ml. glass bulbs provided with stopcocks on either end and standard taper joints for connection to the vacuum line.

In the radical reaction experiments, the reactant gases (tetrafluoroethylene, chlorine or bromine) were condensed on top of the radical deposit before removing the liquid nitrogen. In one experiment, however, chlorine was added to the deposit after warming slightly to bleach the blue but not the red color. After adding the reactant gas, the liquid nitrogen was removed and the deposit warmed as before.

In the halogenation experiments, excess halogen was always added. In order to protect the instruments used for analysis and to prevent reaction of the excess halogen with unsaturated warm-up products, the excess halogen was removed prior to sampling. This was done by connecting a small drying tube filled with moist soda-lime in series with the sample bulbs. The excess halogen was thus removed immediately before sampling so that the contact time of excess halogen with warm-up products was less than 60 seconds after evaporating the deposits.

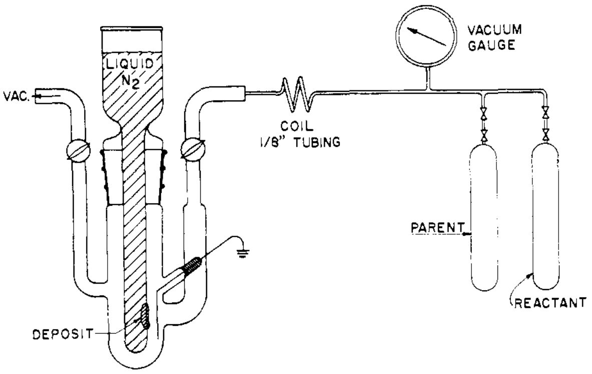


Fig. 1.—Free radical trap and flow lines.

Three analytical instruments were used for identification and analysis of the product gases. These were a General Electric Model G.E. V mass spectrometer, a Bendix Time-of-Flight mass spectrometer coupled with a Perkin-Elmer and/or a Burrell Model K-1 gas chromatograph, and a gas chromatograph sensitive to p.p.m. concentrations.

The chlorination and disproportionation products of captive radicals obtained from $C\text{–}C_4F_8$ and the disproportionation products of captive radicals obtained from C_2F_6 were positively identified by observed cracking patterns obtained with the Bendix mass spectrometer. The components of each mixture were first separated with the Perkin–Elmer or the Burrell gas chromatograph and each pure component was then admitted separately into the Bendix mass spectrometer. Analysis of the cracking patterns of the separated components not only simplified the procedure but added considerable certainty to their identification. The chromatographic columns used and the retention times observed are listed in Table I. Unfortunately, the chlorination product, CF_3Cl, could not be separated from the C_2F_6 parent gas on any of a dozen or so columns tested. Its identification is based on the usual mass spectrometric analysis of mixtures.

All of the products present in concentrations above 0.1 mole % were detected by means of the ordinary mass spectrometric technique using the General Electric spectrometer. The quantitative results listed in the tables are based on analyses obtained with this instrument.

The sensitive gas chromatograph used was a 10-meter column of di-(*n*)-butyl maleate on chromosorb which was operated at room temperature with 50 cc./min. helium sweep-gas. The traces of fluorocarbon gases reported were based on retention times of reference compounds against which the column was calibrated. These were as follows

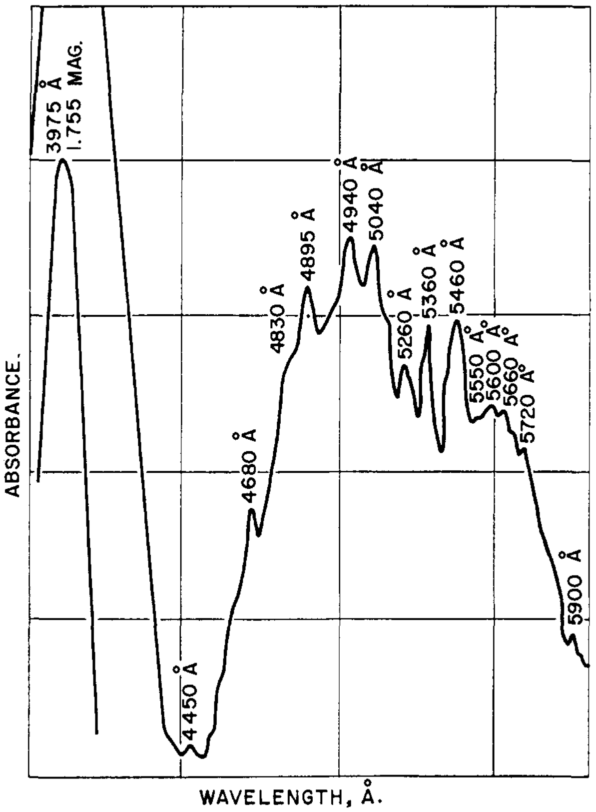


Fig. 2.—Visible spectrum of captive $CF_3\cdot$ radicals from C_2F_6.

for the product gases detected in this way: fluorobutanes at 9'51," fluorohexanes at 11'30" and fluorobutenes or fluoroisobutenes at 15'28". On this column, C_2F_6 had a retention time of 8'0" and C_2F_4 came off at 8'30". These were well in advance of the major products. Of course, there is still some uncertainty in the identity of these compounds since gas chromatography, when used alone, always permits the possibility of other compounds with the same retention time. The identity of these trace products, however, was considered to be of secondary importance in this work.

Although calibration of the analytical instruments was based on volume per cent. the values reported correspond to mole per cent. within the accuracy of the instruments. This is true of all the results which follow unless otherwise stated.

Experimental

1. **Hexafluoroethane Experiments.**—Passage of an electric discharge through hexafluoroethane flowing at a rate of 10–20 g./hr. produced a salmon-red deposit in 15 minutes on the liquid nitrogen finger. The red color persisted at liquid nitrogen temperature for several hours with no apparent change. On warming, it changed abruptly to white at 107 ± 5°K. No polymer residue was left on evaporation and mass spectrometric analysis of the gas showed only hexafluoroethane, the parent compound. These results are recorded in Table II, experiment number 2.1.

When chlorine was added to the red deposit at 77°K. and the product gases analyzed after warm-up, only CF_3Cl was obtained in concentrations ranging from 0.3 to 0.7% plus parent compound. No polymer residue was observed. This result is recorded in Table III, experiment 3.1.

When tetrafluoroethylene gas was condensed on top of the red deposit at 77°K. and it was allowed to warm, it turned light yellow. This color faded near the melting point, and, on evaporation, 0.05 to 0.1 g. of a fusible polymer was obtained as a residue. The polymer was identified as polytetrafluoroethylene by infrared analysis and melting point (~ 327°). The warm-up products in the gas were identified as 0.2% of $CF_3CF{=}CF_2$ and 0.2% of CF_3CF_2-CF_3 (?). Traces, in parts per million (p.p.m.), of perfluorobutynes, perfluorobutenes and perfluorohexanes were identified by vapor phase chromatography as previously described. These results are listed in Table II, experiment 2.2.

On extending the radical generation time to 30 minutes or longer, the center of the red deposit bleached and turned green. The green color was also observed in transmitted light. On warming, the colors faded, as usual, and after evaporation, a small polymer residue was observed. Mass spectrometric analysis of the gas revealed the presence of 0.5 to 1.5% CF_4, 0.3% $CF_3CF_2CF_3$ and possible traces of $CF_2{=}CF_2$. The identification of these three gases was confirmed by individual cracking patterns. The gaseous mixture was first subjected to gas chromatography (see Table I, 1.5 meter squalane on silica gel) and the separated components fed directly into the Bendix mass spectrometer as described previously. The results of this experiment are recorded in Table II, experiment 2.3.

2. **Octafluorocyclobutane Experiments.**—Passage of an electric discharge through octafluorocyclobutane with a rate of flow of 10–20 g./hr. produced an ink-deep prussian blue deposit on the liquid nitrogen finger in a few minutes. The blue color persisted for several hours with no apparent change at liquid nitrogen temperatures. On warming, the blue color faded abruptly at 95 ± 5°K. to a light pink color which finally turned white at 107°K. on further warming. No polymer residue was observed on evaporation and mass spectrometric analysis revealed 0.2 to 1.2% $CF_2{=}CF_2$ as the major warm-up product with possible traces of C_2F_6. Vapor phase chromatography showed that p.p.m. quantities of fluorohexanes were also present. These results are summarized in Table II, experiment 2.4.

When chlorine was condensed on top of the blue deposit at 77°K. and the warm-up products analyzed by mass spectrometry, 0.7% CF_3Cl, 2.3% CF_2Cl_2, 1.1 ± 0.1% CF_2Cl_2-CF_2Cl_2 and possible traces of CF_3CF_2Cl were detected. CF_3Cl, CF_2Cl_2 and CF_2ClCF_2Cl were identified by their observed cracking patterns, by separation on a vapor phase column and by admitting the isolated compounds directly to the Bendix TOF mass spectrometer as previously described (see Table I, first two runs). No polymer residue was observed. These results are recorded in Table III, experiment 3.2.

When the radical generation period was extended to more than 10 to 15 minutes, a small red spot formed near the center of the prussian blue deposit. The red spot then spread in size to about 1.25 inches in diameter within a few seconds. This matched the 1.25 inch opening of the feed line into the body of the trap and was directly opposite to it on the cold finger. Both the red and the blue colors were apparently pure in reflected and in transmitted light. This indicated that the original blue color in the center had changed to red and that a red color had not simply deposited on top of the original blue color. The red spot was covered in some regions by dark patches which may have been carbon. On warming, both colors bleached near their respective transition temperatures, first the blue (95°K.) and then the red (107°K.). A gray or brown polymer residue (0.05–0.10 g.) remained after evaporation.

When chlorine was condensed on top of the multicolored deposit at 77°K., mass spectrometric analysis of the product gases revealed 3.4 ± 0.3% CF_3Cl, 0.35 ± 0.1% CF_2Cl_2 and 0.65 ± 0.1% CF_2ClCF_2Cl (Talbe III, experiment 3.3). When bromine was added to a similar deposit, mass spectrometric analysis revealed 2.6 ± 1.0% CF_3Br, 0.15 ± 0.1% CF_2Br_2 and 0.75 ± 0.2% CF_2BrCF_2Br (Table III, experiment 3.4). No polymer residue was observed in these halogenation experiments.

Since the red- and blue-colored species had different fading temperatures, chlorination of the remaining red-colored matrix could be effected after causing the blue-colored species to fade by warming the deposit to temperatures above 95°K. A blue deposit was generated from C–C_4F_8 and the generation time was extended to the point where the red spot

TABLE I

CHROMATOGRAPHIC COLUMNS USED WITH BENDIX MASS SPECTROMETER

Column description		Conditions			
Length, m.	Adsorbent	He, cc./min.	Temp., °C.	Parent gas	Retention time of components, sec.
10.0	20% di-*n*-butyl maleate on chromosorb (Johns–Manville, 30–85 mesh)	30	28	C–C_4F_8	CF_2Cl_2 (510), CF_2ClCF_2Cl (675)
1.0	2% squalane on silica gel (40–60 mesh)	100	50	C–C_4F_8	$CF_3$3l (150)
1.5	3% squalane on silica gel (40–60 mesh)	100	25	C–C_4F_8	Air (25), CF_4 (40), C_2F_6 (155), C_2F_4 (240)
1.5	3% squalane on silica gel (40–60 mesh)	100	25	C_2F_6	Air (25), CF_4 (40), C_3F_8 (660)

TABLE II

WARM-UP AND TETRAFLUOROETHYLENE ADDITION PRODUCTS OF CAPTIVE RADICALS

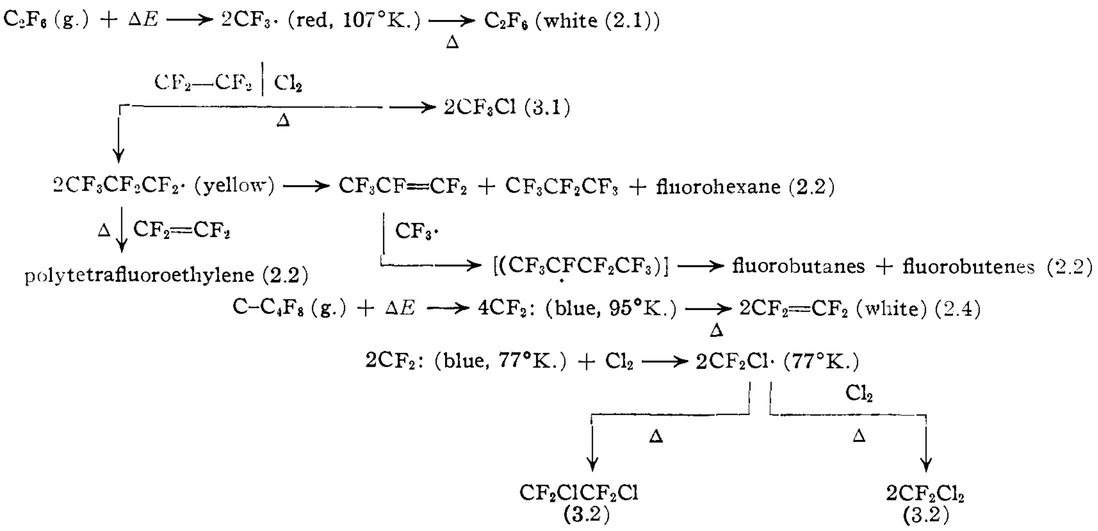
Expt. no.	Generation time, min.	Deposit after generation	Bleaching temp., °K.	Parent gas	Reactant gas	Deposit after reaction	No. of expts.	Major products (vol. %)	Minor products, p.p.m.	Comments
2.1	15	Red field	107 ± 5	C_2F_6	None	....	2	None	None	No polymer residue
2.2	15	Red field	.....	C_2F_6	$CF_2=CF_2$	Yellow on thawing	2	$CF_3CF=CF_2$ (0.2) $CF_3CF_2CF_3$ (0.2)	Perfluorobutenes Perfluorobutanes Perfluorohexanes	0.05–0.10 g. polymer residue
2.3	>30	Green spot on a red field	.....	C_2F_6	None	....	2	CF_4 (0.5–1.5) $CF_3CF_2CF_3$ (0.3)	$CF_2=CF_2$	Red deposit changed to one with a large green spot. Some polymer formed
2.4	10–15	Blue field	95 ± 5	C–C_4F_8	None	....	2	$CF_2=CF_2$ (0.2–1.2)	C_2F_6, perfluorohexanes	The blue color faded at 95°K. into a pink color which persisted up to 107°K. before final bleaching
2.5	30–45	Faded pink spot on a blue field	.....	C–C_4F_8	None	....	2	CF_4 (0.5–1.5) C_2F_6 (0.1–0.2) $CF_2=CF_2$ (0.7–1.2)	....	Red spot on a blue field faded after spreading to $1^1/_4$ inches in diameter. Some polymer formed

TABLE III

PRODUCTS OF HALOGENATION OF CAPTIVE RADICALS

Experimental conditions						Halogenation products[a]								Average radical yields — per cent of total yield[b]	
						Volume per cent.				Per cent. of total product					
Expt. no.	Generation time, min.	Deposit before halogenation	Halogenation temp., °K.	Parent compound	No. of expt.	CF_3X	CF_2X_2	CF_2XCF_2X	$CF_2=CF_2$	CF_3Cl	CF_2Cl_2	CF_2XCF_2X	$CF_2=CF_2$	$CF_3\cdot$ Radical	$CF_2:$ Radical
3.1	15	Red field	77, Cl_2 added	C_2F_6	4	0.5 ± 0.2	....	....	....	100.0	..	..	..	100	0
3.2	10–15	Blue field	77, Cl_2 added	C–C_4F_8	2	0.7 ± .0	2.3 ± 0.0	1.1 ± 0.1	....	17.1	56.1	26.8	..	13	87
3.3	15–30	Large red spot on a blue field	77, Cl_2 added	C–C_4F_8	2	3.4 ± .3	0.35 ± .1	0.65 ± .1	....	77.3	8.0	14.7	..	67	33
3.4	15–30	Large red spot on a blue field	77, Br_2 added	C–C_4F_8	5	2.6 ± 1.0	0.15 ± .1	0.75 ± .1	....	74.3	4.3	21.4	..	59	41
3.5	10–15	Blue color bleached, red color persists	95–107, Cl_2 added	C–C_4F_8	2	1.1 ± 0.6	....	....	0.3 ± 0.1	78.6	..	..	21.4	65	35

[a] X = Cl or Br. [b] Note that 2 moles of CF_2: radical yield only 1 mole of CF_2ClCF_2Cl or $CF_2=CF_2$ in a stoichiometric equation.



started to form. At this point, the flow of gas and the electrical discharge was stopped. The liquid nitrogen was siphoned out of the cold finger and the red and blue deposit was allowed to warm slowly until the blue color faded and only a pink color around the red spot remained. At this point, 1 to 2 g. of chlorine gas was added quickly to the system and allowed to condense on the pink and red deposit. The deposit was then melted and evaporated and the vapors collected. Mass spectrometric analyses of the product gases revealed 0.4 to 1.7% CF_3Cl and 0.2 to 0.4% $CF_2{=}CF_2$ as the only gaseous products (Table III, experiment 3.5). No polymer residue was observed.

When the radical generation period was extended beyond 30 minutes, the red center faded, but the blue field persisted. After evaporation, a polymer residue was noted. Mass spectrometric analysis of the product gases revealed the presence of 0.7 to 1.2% $CF_2{=}CF_2$, 0.1 to 0.2% C_2F_6 and 0.5 to 1.5% CF_4 (Table II, experiment 2.5). The identity of these gases was confirmed by individual cracking patterns as previously described (Table I, third row).

3. Some Physical Properties of the Radicals. A. Color Transition Temperatures.—A thermocouple was wrapped around the cold finger and the fading temperatures were measured for the red deposit from hexafluoroethane and the blue deposit from perfluorocyclobutane. The red deposit faded abruptly at 107 ± 5°K., while the blue deposit faded abruptly at 95 ± 5°.

B. Visible Spectrum.—For the purpose of obtaining qualitative spectra, the radicals were deposited on a square finger in a trap which could be removed from the vacuum line. A Model 14 Cary Spectrophotometer was used. The thickness of the deposit and the concentration of radical species was not measured. Therefore, extinction coefficients were not obtained. The spectrum of the red deposit is shown in Fig. 2. This was repeated four times with four fresh deposits. The same spectrum was obtained each time.

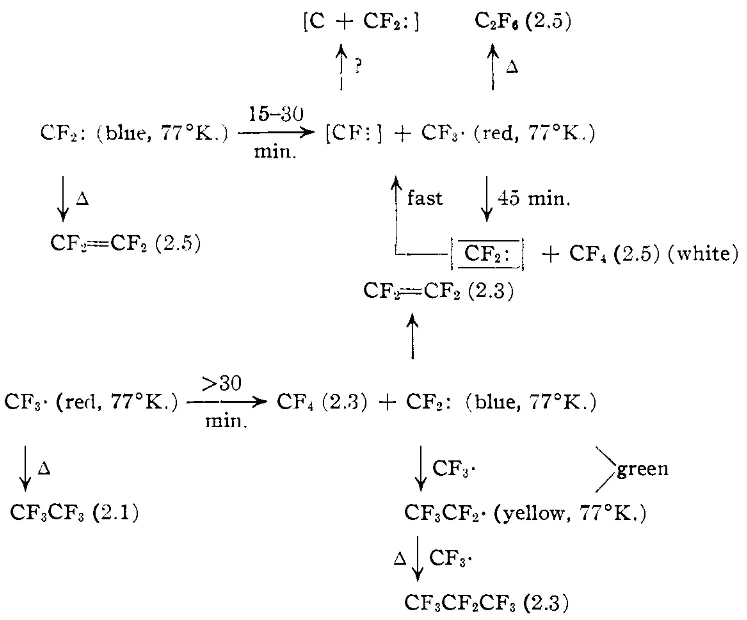
No detailed spectrum of the blue deposit was obtained because optical density was always excessive. However, large bands were observed at 5050, 5650 and 7000–7500 Å.

Discussion of Results

Interpretation of these results is based on the halogenation and warm-up products. CF_3Cl was always the only halogenation product when the red color was present alone (experiments 3.1 and 3.5). The simplest explanation is that this product results from reaction of captive $CF_3\cdot$ radicals with chlorine. The $CF_3\cdot$ radical is therefore associated with the red deposit.

Chlorination of the blue deposits from octafluorocyclobutane produced a mixture of CF_3Cl, CF_2Cl_2 and CF_2ClCF_2Cl, with a possible trace of CF_3CF_2Cl. Fortunately, the fading temperatures of the two colors were sufficiently different (12°) to allow a chlorination of the pink residue after the blue color faded at 95°K. (experiment 3.5). In this experiment, CF_3Cl and $CF_2{=}CF_2$ were the sole products present in addition to parent compound. The simplest interpretation of these results is that the apparently pure blue color is actually a mixture of blue and red and that the blue species has a much greater extinction coefficient. This was borne out by attempts to obtain the absorption spectra previously described. Hence, if the CF_3Cl product, associated with the red color, is subtracted from the results of experiments 3.2 and 3.5, the products which remain are most easily explained on the basis of reaction of CF_2: with chlorine to form $CF_2Cl\cdot$ radicals. These either react with more chlorine to form CF_2Cl_2 or combine to form CF_2ClCF_2Cl. Combination of CF_2: in the absence of halogen would form $CF_2{=}CF_2$, as was the case in experiment 3.5. The absence of CF_2ClCF_2Cl in experiment 3.5 lends support to formation of this product through combination of the $CF_2Cl\cdot$ radical rather than through the simple addition of Cl_2 to $CF_2{=}CF_2$. Removal of the excess halogen immediately after melting the deposit and prior to sampling precluded reaction of halogen in the gas phase. It is concluded therefore that the blue deposit obtained from $C{-}C_4F_8$ is mainly associated with the CF_2: radical.

This identification of the deposits is also consistent with the warm-up and $CF_2{=}CF_2$ addition products (experiments 2.1, 2.2 and 2.4). Recombination of $CF_3\cdot$ radicals occurs at 107°K. in the C_2F_6 matrix to form C_2F_6, the parent compound. This is consistent with experiment 2.1 in which no products other than the parent compound were detected. Addition of $CF_2{=}CF_2$ to the red deposit from C_2F_6 yielded products consistent with reactions of $CF_3\cdot$ radicals with fluoroölefins as listed in Table II, experiment 2.2. Detection of $CF_2{=}CF_2$ as a warm-up product of the blue deposit from $C{-}C_4F_8$ in experiment 2.4 is consistent with its detection in experiment 3.5 when the blue color was allowed to fade before chlorination. This product is most easily explained by combination of CF_2: radicals associated with the blue deposit.



Reactions of CF_2: and $CF_3\cdot$ radicals which are consistent with the observations are summarized below. The numbers in parentheses refer to experiment numbers listed in Tables II and III.

Contamination of the blue deposit by $CF_3\cdot$ radicals is explained on the basis of radical transformations which are believed to be disproportionations. Although logical coproducts were observed to support this, no quantitative data or material balances were made. However, that radical transformations occur at liquid nitrogen temperatures is borne out not only by the dramatic color changes, from blue to red (2.5, 3.3 and 3.4), red to white (2.5) and red to green (2.3), but also by analysis of the warm-up and halogenation products which again confirm the association of the red color with $CF_3\cdot$ and the blue color with CF_2:. These low temperature transformations support identification of these radicals with their respective colors.

The radical transformations could proceed in any number of ways. One possible mechanism is that of disproportionation. This seems consistent with both the warm-up products produced and the color changes. Apparently, two courses can be written for the disproportionations, depending on the presence of the radical with the highest concentration. Also, it is possible that carbon (dark coloration of polymer produced) can be produced by the disproportionation of CF_2: to $CF_3\cdot$ and [CF:]. The [CF:] may then rapidly disproportionate into carbon and CF_2:. The presence of carbon could influence the reactions by catalysis. This would explain the rapid spreading of the red spot on the blue field once the transformation begins. One possible set of reactions which explains both the color changes and the warm-up products is shown below. The numbers in brackets refer to experiment numbers in Table II.

It is to be noted that although halogenation reaction products from both $CF_3\cdot$ and CF_2: radicals were present in experiments 3.2, 3.3 and 3.4, radical products from $CF_3\cdot$ predominated when the color was red (3.3 and 3.4) as seen from the total volume % quantities listed in Table III. The total volume % quantities (Table III) are normalized values obtained by subtracting out the parent compound. Similarly, radical products from CF_2: predominated when the color was blue (3.2). The total radical concentrations as calculated stoichiometrically from the above reactions schemes although quite high, up to 5% in experiments 3.3 and 3.4, are not inconsistent with theoretical calculations of possible radical concentrations which range up to 6.5%.[7]

It is interesting that products of disproportionation of $CF_3CF_2CF_2\cdot$ and of $(CF_3)_2CFCF_2\cdot$ or $CF_3CF_2CF_2CF_2\cdot$ were found in experiment 1.2. These reactions are energetically feasible[8] but never have been reported in polymerization or radical reactions. In fact, Pritchard and Miller[9] exclude it from consideration in their analysis of C_3F_7 recombination and hydrogen abstraction studies. It must be remembered, however, that the C_3F_7 radicals reported in this work may still be partially immobilized and isolated from each other by solid solution or dispersion in the matrix of excess parent compound after they form by reaction of the more mobile $CF_3\cdot$ with $CF_2{=}CF_2$. This consideration alone would preclude radical recombination until the point at which the matrix actually melts. Further complications no doubt result from third body considerations in the melt.

The double disproportionation of CF_2: to $CF_3\cdot$ and carbon, followed by disproportionation of $CF_3\cdot$ to CF_4 and CF_2: is unique. Both reactions are energetically feasible[8] again on the basis of the stability of the final products or coproducts. It is difficult to say, therefore, which is the more stable in a solid matrix, CF_2: or $CF_3\cdot$.

Another interesting point is the absence of $ClCF_2CF_2CF_2CF_2Cl$ in any of the halogenation products

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[7] P. L. Chessin, *J. Chem. Phys.*, **31**, 159 (1959).

[8] W. M. D. Bryant, private communication to be published.

[9] G. O. Pritchard and G. H. Miller, *J. Phys. Chem.*, **63**, 2074 (1959).

in the octafluorocyclobutane experiments. The first step in the formation of CF_2: from this parent must involve scission of a carbon–carbon bond. The butane diradical thus formed and all intermediate diradicals must be extremely unstable. Apparently, the butane diradical either reverts quickly back to the parent compound or it completely unzips to CF_2:

Finally, an interesting consideration in this work is the possible presence of species other than CF_2: and $CF_3\cdot$ which could lead to the same chlorination and warm-up products observed. For example, can CF_2: exist in singlet and/or triplet states? We have recently acquired some preliminary gas phase data which favors the existence of both states and assigns the ground state to the singlet. This same evidence indicates that the captive CF_2: radicals studied in this work are not in the ground singlet state as might be expected but are rather in some excited triplet state. This should be regarded as preliminary information which we plan to investigate more thoroughly in the near future. Another possibility is the presence of ions and radical-ions such as CF_3^+ and $CF_2\cdot^+$. These could certainly explain the halogenation and warm-up products as easily as the pure radicals. However, it is felt that their presence in high concentration is unlikely because: (1) The plasma in which they are created probably contains these ions initially, but on the average, the plasma contains just as many electrons which would neutralize the ionic charge in the matrix (it is highly unlikely that electrons would be trapped along with the ions). (2) Build-up of a space charge about the cold finger due to accumulation of ions would cut down the efficiency in time. No such effect was noticed. (3) A metal spatula cooled to liquid nitrogen temperatures and placed in contact with the deposit does not seem to discharge it or affect it in any way.

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Microwave Absorption and Molecular Structure in Liquids. XLVI. The Apparent Dipole Moments of Several Symmetrical Molecules[1,2]

BY ERNEST N. DICARLO[3] AND CHARLES P. SMYTH

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The dielectric constants and losses at wave lengths of 1.25 and 3.22 cm. and 575 m. have been measured for hexachlorobenzene, hexamethylbenzene and 4,4'-dinitrobiphenyl in benzene solution at 20°, *p*-dinitrobenzene in benzene solution at 25° and iron pentacarbonyl as the pure liquid at 20°. Dielectric constant and loss measurements have also been made at wave lengths of 3.22 cm. and 575 m. on benzene solutions of phenanthrene and chloranil at 40°, anthraquinone and *p*-benzoquinone at 50° and tetramethyl-1,3-cyclobutanedione at 20°. The dielectric constant and loss were also measured at 3.22 cm. wave length for *p*-benzoquinone in benzene solution at 20°. The results were used to calculate upper limits to the permanent dipole moments of the above molecules. The absence of frequency dependence of the dielectric constant data excludes any dipole moment values greater than approximately 0.5 *D*, while the absorption data exclude any values greater than 0.10 or 0.20 *D*, depending upon the concentration of the solution measured.

This study was undertaken because many careful dielectric constant measurements at radio frequencies have indicated the possession of small but appreciable dipole moments for supposedly symmetrical molecules.[4,5] Whether a molecule has a permanent dipole moment or not can be determined by measuring the frequency dependence of the dielectric constant and loss in the region where anomalous dielectric dispersion should occur if the molecule were polar.[6] In this frequency region, the dielectric constant of a polar liquid decreases with increasing frequency with most of the decrease occurring within a 100-fold frequency range. In this same range, the dielectric loss changes from a small value through a maximum to a small value again. The loss factor due

TABLE I

SOURCES, METHODS OF PURIFICATION, MELTING POINTS AND REFRACTIVE INDEX

Compound	Source	M.p., °C.
p-Dinitrobenzene[a]	A	175.0–175.8
Hexachlorobenzene[a]	A	230.2–231.0
Chloranil[a]	A	294.2–294.6 (sealed tube)
Hexamethylbenzene[a]	B	166.3–167.0
4,4'-Dinitrobiphenyl[a]	B	239.8–240.6
Anthraquinone[a]	B	284.8–285.6 (sublimes)
Tetramethylcyclobutanedione[a]	B	114.5–114.9
Phenanthrene[b]	B	102.6–103.9
p-Benzoquinone[d]	C	113.4–113.5 n_D 19.7°
Iron pentacarbonyl[c]	D	1.51705

[a] Repeated crystallization from benzene and drying under vacuum over phosphorus pentoxide in an Abderhalden pistol. [b] Repeated crystallization from benzin (60–70°) and drying under vacuum over phosphorus pentoxide in an Abderhalden pistol. [c] Fractionally distilled. [d] Repeated crystallization from 95% ethanol. Purified by G. F. Wright.

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[2] This paper represents part of the work submitted by E. N. DiCarlo to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Esso Foundation Fellow, 1960–1961. National Science Foundation Summer Fellow, 1961.

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[5] P. Podleschka, L. Westland and G. F. Wright, *Can. J. Chem.*, **36**, 574 (1958).

[6] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, New York, N. Y., 1955, Chap. II.