[Contribution from the Baker Laboratory of Chemistry, Cornell University]

# The Mechanism of Fluorination. II. Free Radical Initiation Reactions. Fluorine-sensitized Chlorination and Oxidation

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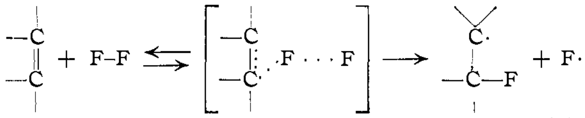
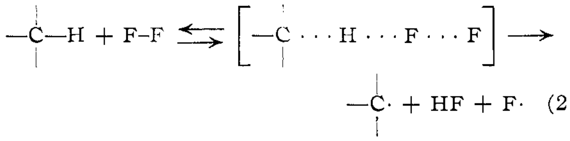
Evidence is presented for the reaction of elemental fluorine with olefins to produce a fluorinated free radical and a fluorine atom (1), and for the reaction with carbon-hydrogen bonds to produce a free radical, hydrogen fluoride and a fluorine atom (2). These reactions consist of one-electron displacements on the fluorine molecule. This view of the mechanism of attack by fluorine is consistent with the products obtained from tetrachloroethylene and pentachloroethane, and with the products obtained when fluorine is used as a free-radical type promoter for reactions with chlorine and oxygen. The molecular free-radical initiation reactions that lead to the production of pairs of radicals can account for the formation of saturated and unsaturated products in which no fluorine is introduced, as well as fluorinated substitution and addition products. The mechanisms discussed furnish a satisfactory basis for correlating the diverse reactions of fluorine with organic compounds.

## Introduction

Reactions between fluorine molecules and organic systems to yield free radicals, as shown below, require that under suitable conditions fluorine should serve as an initiator for various free radical chain reactions. Experimental evidence for the occurrence of reaction 1 is derived from the use of elemental fluorine in small amounts at 0 and −15° to promote the reactions of trichloro- and tetrachloroethylene with oxygen.[1] It is to be expected also on the basis of reactions 1 and 2 that fluorine should be capable of acting as a promoter for free-radical type reactions with chlorine. This has been shown by McBee and Bittles,[2] who found as a preparative procedure that the vapor phase chlorination of ethane was initiated by fluorine at room temperature or lower and that a variety of organic compounds including *n*-hexane, *n*-pentane and benzene could be chlorinated by dissolving them in liquid chlorine and passing in fluorine.



(1)



$$-\overset{|}{\underset{|}{C}}-H + F-F \rightleftarrows \left[-\underset{|}{C}\cdots H\cdots F\cdots F\right] \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + HF + F\cdot \quad (2)$$

In the present paper, which is concerned principally with reaction 2, the fluorine-sensitized reactions of chlorine with tetrachloroethylene and with pentachloroethane, and the fluorine-sensitized oxidation of pentachloroethane are reported. Tetrachloroethylene and pentachloroethane provide relatively simple experimental cases for investigation and their reactions with fluorine alone have been studied previously.[3] The results of these and other reactions between elemental fluorine and organic compounds are examined as tests of reactions 1 and 2.

## Experimental

**Fluorine–sensitized Chlorination of Tetrachloroethylene.**—Reactions were carried out in a one-liter three-necked flask which was fitted with a glass thermocouple well, a 0.25″ copper fluorine inlet tube extending just into the body of the flask, a glass gas-tight stirrer, and a 1-cm. outlet tube leading from about 0.5 cm. above the liquid surface of the stirred liquid to a Dry Ice cooled trap. Closures were made with rubber stoppers impregnated with ceresin wax and covered with copper foil. Metal stopcocks used for fluorine and nitrogen connections to the fluorine line were lubricated with Kel-F type chlorofluorocarbon grease.

After purification by washing with concentrated sulfuric acid and distillation, 466 g., 2.81 moles, of tetrachloroethylene was placed in the reaction flask, cooled to −7° with an ice–salt-bath, and 1.07 moles of chlorine added. Air was displaced from the reaction flask with dry nitrogen and a nitrogen blanket maintained at the outlet from the cold trap. Fluorine produced in our previously described cell[4] was passed into the reaction mixture for 98 minutes at an electrolysis current of one ampere, with an experimentally determined current efficiency of 90%, corresponding to a total of 0.023 mole of fluorine. The reaction appeared to be inhibited for the first 80 minutes after which the temperature rose suddenly from −6 to +41° in seven minutes. Most of the reaction appeared to take place during this period and the temperature had fallen back to 3° when the reaction was discontinued. Crystalline material was present in the reaction mixture. Separation by distillation and sublimation and by crystallization from methanol yielded 0.3 g. of *sym*-tetrachlorodifluoroethane, b.p. 90–94°, m.p. 12–15°; 302 g., 1.82 moles, of recovered tetrachloroethylene, b.p. 118.4–118.5° at 729 mm.; 3.6 g., 0.016 mole, of pentachlorofluoroethane, m.p. 97°; 215 g., 0.91 mole, of hexachloroethane, m.p. 184–185° in a sealed tube, corresponding to 85% of the chlorine utilized. Previously reported: *sym*-tetrachlorodifluoroethane, b.p. 92.8°, m.p. 24.65°[5]; pentachlorofluoroethane, m.p. 101.3°[5]; hexachloroethane, triple point 186.8°.[6] Titration of the tetrachloroethylene fraction with alkali gave values corresponding to less than 1 g. of trichloroacetyl chloride.

**Fluorine-sensitized Chlorination of Pentachloroethane.**—Redistilled pentachloroethane was further purified by partial freezing to yield material, b.p. 161.0–161.1° at 741.5 mm., calcd. 162.0–162.1° at 760 mm.,[7] f.p. −28.6°, $n^{20}\text{D}$ 1.5028, $d^{20}_4$ 1.6806; previously reported: b.p. 162.00° at 760 mm., f.p. −29.0°, $n^{20}\text{D}$ 1.50312, $d^{20}_4$ 1.68063.[7] Fluorine prepared as indicated above and freed from hydrogen fluoride by passing through a Dry Ice cooled trap and sodium fluoride packed copper tube was used to fill a brass 2-l. tank at atmospheric pressure by flushing to displace nitrogen. The tank was then pressured with Linde 99.99% nitrogen to 195 p.s.i. gage. The tank was constructed from 3.5″ o.d. heavy-walled brass pipe with threaded and silver soldered caps, and was fitted with Hoke Monel needle valves, with Teflon packings, at each end and a calibrated 200-lb. Ashcraft pressure gage with silver-soldered bronze Bourdon tube. The composition of the fluorine–nitrogen mixture was determined before and after reaction by treatment of 5 p.s.i.

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(1) W. T. Miller, Jr., and A. L. Dittman, This Journal, **78**, 2793 (1956).

(2) E. T. McBee, *Ind. Eng. Chem.*, **40**, 1612 (1948); unpublished experimental work with J. A. Bittles.

(3) W. T. Miller, Jr., This Journal, **62**, 341 (1940).

(4) W. T. Miller, R. L. Ehrenfeld, J. M. Phelan, M. Prober and S. K. Reed, *Ind. Eng. Chem.*, **39**, 401 (1947).

(5) E. G. Locke, W. R. Brode and A. L. Henne, This Journal, **56**, 1726 (1934).

(6) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950.

(7) J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 755 (1926).

aliquots with an aqueous potassium iodide solution followed by titration with thiosulfate of the iodine set free.

From the tank the fluorine–nitrogen mixture was passed through a Pyrex bubble counter filled with Kel-F type chlorofluorocarbon oil which was attached to 0.25″ copper tubing with ground-in sleeve connections sealed on the outside with ceresin wax. Matheson chlorine was added to the fluorine line through a capillary type flow meter. The reaction flask was arranged as described above for tetrachloroethylene and immersed in a mechanically stirred heated oil-bath.

For reaction, 607.3 g., 3.00 moles, of pentachloroethane was placed in the reaction flask saturated with chlorine at 100° and the fluorine–nitrogen mixture plus chlorine added with the rates of gas flow so adjusted that the ratio of chlorine to fluorine was 100. In this way 0.0205 mole of fluorine and 2.06 moles of chlorine were added during six hours and 51 minutes with efficient stirring and the temperature maintained at 97–105°. Reaction occurred smoothly.

Separation of the 626.8-g. reaction product by distillation and crystallization yielded 399 g., 1.97 moles, of recovered pentachloroethane, and 176 g., 0.743 mole, of hexachloroethane. Pentachlorofluoroethane could not be isolated, but analysis for fluorine of the pentachloroethane which distilled first indicated the presence of 0.87 g., 0.0043 mole. Only trace amounts of oxidized products were indicated by alkali titration.

**Fluorine-sensitized Oxidation of Pentachloroethane.**—The apparatus described above for the chlorination of pentachloroethane was utilized for reaction. Oxygen was substituted for nitrogen to prepare a fluorine–oxygen mixture in the ratio of 1:49 at 170 p.s.i. gage pressure.

The reaction flask was charged with 202.3 g., 1.00 mole, of pentachloroethane from the same batch described above and a fluorine–oxygen mixture containing 0.018 mole of fluorine and 0.882 mole of oxygen passed in during five hours and 49 minutes with the heating bath maintained at 97–105°. The colorless reaction product was analyzed by distillation and titration as previously described[1] and found to contain: 164.3 g., 0.812 mole, of recovered pentachloroethane; 0.020 mole of carbonyl chloride, corresponding to 0.010 mole of pentachloroethane, identified by the anilide, m.p. 234–235°; 0.099 mole of trichloroacetyl chloride, identified by the anilide, m.p. 91–92°. Previously reported: *sym*-diphenylurea, m.p. 238–239°;[8] trichloroacetanilide, m.p. 94–95°.[9]

## Results and Discussion

**Fluorine-sensitized Chlorination and Oxidation.** Leermakers and Dickinson[10] working with carbon tetrachloride solutions at room temperature found that the photochemical reaction of chlorine with tetrachloroethylene was strongly inhibited by dissolved oxygen. Only oxidation occurred with a quantum yield close to unity until the oxygen was consumed, at which point the addition of chlorine proceeded with high quantum yield. In the present work analogous results were obtained with elemental fluorine in place of photochemically produced chlorine atoms. The total amount of fluorine used was equivalent to about 2% of the chlorine present, but most of this was consumed during the induction period. Hexachloroethane was isolated in high yield together with a small amount of pentachlorofluoroethane and a trace of *sym*-difluorotetrachloroethane. These results are consistent with free radical initiation in accordance with reactions 3 and 5, followed by 6 and the usual chain propagation steps with chlorine (7 and 8). As a maximum

$$CCl_2{=}CCl_2 + F_2 \longrightarrow CCl_2FCCl_2\cdot + F\cdot \qquad (3)$$

$$CCl_2FCCl_2\cdot + F\cdot \longrightarrow CCl_2FCCl_2F \qquad (4)$$

$$CCl_2{=}CCl_2 + F\cdot \longrightarrow CCl_2FCCl_2\cdot \qquad (5)$$

$$CCl_2FCCl_2\cdot + Cl_2 \longrightarrow CCl_2FCCl_3 + Cl\cdot \qquad (6)$$

$$CCl_2{=}CCl_2 + Cl\cdot \longrightarrow CCl_3CCl_2\cdot \qquad (7)$$

$$CCl_3CCl_2\cdot + Cl_2 \longrightarrow CCl_3CCl_3 + Cl\cdot \qquad (8)$$

$$CCl_2FCCl_2\cdot + F_2 \longrightarrow CCl_2FCCl_2F + F\cdot \qquad (9)$$

$$CCl_3CCl_2\cdot + F_2 \longrightarrow CCl_3CCl_2F + F\cdot \qquad (10)$$

one fluorine molecule can initiate two reaction chains. The formation of carbon–fluorine bonds occurs to a very minor extent (4, 9 and 10). Termination reaction 4 is indicated because of the production of the reactants in pairs by reaction 3. Pairing reactions involving chlorine atoms, and chlorine atoms and free radicals are more important termination processes.

The photochemical chlorination and chlorine-sensitized oxidation of pentachloroethane have been investigated in the vapor phase at 80–100° by Schumacher and Thürauf.[11] With small amounts of added oxygen complete inhibition of chlorination comparable to that observed with tetrachloroethylene was not found. However, with increasing concentration of oxygen, trichloroacetyl chloride, 90%, and carbonyl chloride, 10%, became the principal products. Results were best explained by a free-radical chain mechanism, (11) to (16), which is very similar to that proposed for the chlorine-sensitized oxidation of tetrachloroethylene.[12]

Initiation

$$Cl_2 + h\nu \longrightarrow 2Cl\cdot \qquad (11)$$

$$CCl_3CHCl_2 + Cl\cdot \longrightarrow CCl_3CCl_2\cdot + HCl \qquad (12)$$

Chlorination

$$CCl_3CCl_2\cdot + Cl_2 \longrightarrow CCl_3CCl_3 + Cl\cdot \qquad (13)$$

Oxidation

$$CCl_3CCl_2\cdot + O_2 \longrightarrow CCl_3CCl_2O_2\cdot \qquad (14)$$

$$CCl_3CCl_2O_2\cdot \begin{cases} \xrightarrow{a} CCl_3COCl + ClO\cdot \\ \xrightarrow{b} 2COCl_2 + Cl\cdot \end{cases} \qquad (15)$$

$$CCl_3CHCl_2 + ClO\cdot \longrightarrow CCl_3COCl + HCl + Cl\cdot \qquad (16)$$

As predicted on the basis of reaction 2 and the photochemical work summarized above, fluorine was found to sensitize the chlorination and oxidation of pentachloroethane. The reaction of a 1:100 fluorine–chlorine mixture with excess pentachloroethane at 97–105° yielded hexachloroethane and a small amount of pentachlorofluoroethane. The latter, presumably formed by reactions 10 and 18, represented a loss of fluorine available for initiation by reactions 17 and 19.

$$CCl_3CHCl_2 + F_2 \longrightarrow CCl_3CCl_2\cdot + HF + F\cdot \qquad (17)$$

$$CCl_3CCl_2\cdot + F\cdot \longrightarrow CCl_3CCl_2F \qquad (18)$$

$$CCl_3CHCl_2 + F\cdot \longrightarrow CCl_3CCl_2\cdot + HF \qquad (19)$$

The calculated *minimum* average chain length for chlorination was 20, on the basis of two chains for each fluorine molecule, corresponding to a quantum yield of 40.

In the fluorine-sensitized reactions with chlorine, reaction between chlorine and fluorine does not appear to be important. Ruff and his associates found it necessary to heat chlorine and fluorine together at 250° in order to obtain smooth reaction in

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(8) G. Young and E. Clark, *J. Chem. Soc.*, **73**, 367 (1898).

(9) R. Anschütz and A. R. Haslam, *Ann.*, **253**, 129 (1889).

(10) J. A. Leermakers and R. G. Dickinson, THIS JOURNAL, **54**, 4648 (1932).

(11) H. J. Schumacher and Thürauf, *Z. physik. Chem.*, **A189**, 183 (1941).

(12) See reference 1 for a summary.

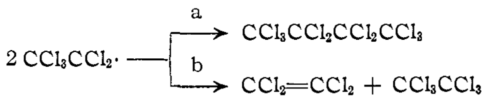
preparing the chlorine fluorides.[13] Fluorine atom reactions with either chlorine or hydrogen chloride with the production of chlorine atoms would lead to chain transfer rather than to chain breaking.

Under the same conditions utilized for chlorination, but with 1:49 fluorine–oxygen in place of the fluorine–chlorine mixture, pentachloroethane gave trichloroacetyl chloride and carbonyl chloride. The concentration of oxygen maintained in the liquid phase must have been very much less than that of chlorine in the previous experiment and shorter reaction chains were indicated by a lower conversion. The observed yields of trichloroacetyl chloride and carbonyl chloride, 10:1, were approximately the same as those obtained by Schumacher and Thürauf, 9:1 with quite different reaction conditions. This result may be interpreted as additional support for their proposal that both oxidation products arise through a common intermediate as shown by reaction 15.

The results summarized above for fluorine-sensitized chlorination and oxidation of pentachloroethane are in agreement with the proposed initiation reactions and confirm the free radical nature of the reactions of fluorine with carbon–hydrogen bonds.

**Mechanism of Fluorination Reactions.**—An essential test of the generality of reactions 1 and 2 consists of examining their usefulness for correlating a wide range of pertinent experimental results. In the following necessarily brief discussion an effort is made to apply this test utilizing significant experiments and to develop a consistent basis for interpreting the reactions of elementary fluorine with organic compounds. The characteristic formation of dimer addition products from tetrachloroethylene[3] and other haloölefins[4] in high yields by reaction with fluorine at low temperatures is particularly noteworthy. At 0° tetrachloroethylene yields octachloro-1,4-difluorobutane as a major product. A mechanism for which convincing evidence has been obtained[14] involves reaction 3, followed by very fast reaction of the fluorine atom to produce two fluoroalkyl radicals within a solvent "cage"; combination of these radicals gives the above dimer. Disproportionation and reactions with fluorine also occur to yield the other observed products. No satisfactory alternative mechanism has been found.

The reaction of *sym*-tetrachloroethane and pentachloroethane with fluorine have been investigated by passing fluorine into the stirred liquids. These compounds are considerably less reactive than ethane,[2] and temperatures of 50 and 90° were found desirable for convenient rates of reaction.[3] Pentachloroethane yielded the following relative molar quantities of isolated products: *sym*-tetrachlorodifluoroethane, 0.066; tetrachloroethylene, 0.25; hexachloroethane, 0.32; pentachlorofluoroethane, 1.00; higher boiling residue was shown to contain decachlorobutane, calculated as $C_4Cl_{10}$, 0.055. The formation of these products, including the unexpected tetrachloroethylene, is consistent with initiation by reaction 17, followed by very fast abstraction of a hydrogen from a neighboring molecule by the fluorine atom (19) to produce a pair of pentachloroethyl radicals. The latter can couple to form decachlorobutane, disproportionate to yield tetrachloroethylene and hexachloroethane (20) or react with fluorine to produce pentachlorofluoroethane (9). The small amount of *sym*-tetrachlorodifluoroethane presumably was formed from tetrachloroethylene.



$$2\,CCl_3CCl_2\cdot \begin{cases} \xrightarrow{a} CCl_3CCl_2CCl_2CCl_3 \\ \xrightarrow{b} CCl_2{=}CCl_2 + CCl_3CCl_3 \end{cases} \qquad (20)$$

The above observations furnish an experimental basis for distinguishing between initiation by thermally produced fluorine atoms, a process analogous to photochemically initiated chlorination, and initiation by reaction 2 at 90°. It will be seen that two fluorine atoms produced by thermal dissociation of a fluorine molecule might produce a pair of pentachloroethyl radicals within a solvent cage by rapid abstraction of hydrogen (19). However, this process can occur only in the presence of excess fluorine. The thermal dissociation of fluorine has an activation energy corresponding at least to its bond strength of *ca.* 37 kcal.[15] and the proportion of fluorine atoms to fluorine molecules must always be extremely small.[16] Assuming a normal frequency factor, thermal initiation can account only for very slow rates of reaction at 100° unless multiplied by a chain reaction mechanism. Consequently, thermal initiation would be expected to result almost exclusively in fluorination chains (19 and 10); that is, fluorine-sensitized *fluorination* analogous to the fluorine-sensitized reactions with chlorine and oxygen described above and in contrast to the results actually obtained. On the other hand, reaction 2 with a relatively low activation energy can occur rapidly enough to maintain a very low concentration of molecular fluorine and account for the observed radical pair reactions (20) which occur at a rate equal to the corresponding initiation steps. Under conditions for which reaction 2 is slow, radical pair reactions should be inhibited as shown below.

Similarly, the fluorination of tetrachloroethane, in addition to tetrachlorofluoroethane, yielded pentachloroethane and trichloroethylene, corresponding to disproportionation products of tetrachloroethyl radicals, and a high boiling residue presumably consisting of dimer-type products.[17] Other ex-

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[13] O. Ruff and E. Ascher, *Z. anorg. allgem. Chem.*, **176**, 258 (1928); O. Ruff and H. Krug, *ibid.*, **190**, 270 (1930). Incorrect references to this work have appeared in the literature stating that reaction was carried out at −170°; *C. A.*, **24**, 3722 (1930); H. S. Booth and J. T. Pinkston, Jr., *Chem. Revs.*, **41**, 436 (1947). The relatively high reaction temperature suggests that thermally produced fluorine atoms are required for initiation. Compare reference 27.

[14] W. T. Miller, Jr., and S. D. Koch, 118th Amer. Chem. Soc. Meeting, Sept. 1950, Abstracts of Papers, p. 23L. This work will be presented in paper III of the present series.

[15] R. N. Doescher, *J. Chem. Phys.*, **20**, 330 (1952).

[16] At 127°, taking 35.3 kcal. mole$^{-1}$ for $\Delta E_0^0$, the equilibrium constant for $F_2 \leftrightarrows 2F^\circ$ has been estimated to be $1.3 \times 10^{-14}$; L. G. Cole, M. Farber and G. W. Elverum, Jr., *ibid.*, **20**, 586 (1952).

[17] Bigelow has postulated free radical mechanisms for the above fluorination reactions based on initiation by fluorine atoms produced in low concentration either thermally or catalytically.[18,19] We are in agreement with these proposals as regards the free radical nature of fluorination reactions and the participation of fluorine atoms. However, our reaction temperatures are too low for thermal initiation to be important in competition with reactions 1 and 2. Furthermore we have no evidence for catalytic initiation. Our mechanisms also differ

amples of polymerization by reaction with fluorine[20,21] also may be interpreted on the basis of the combination of radicals produced by dehydrogenation reactions (17 and 19).

Fluorine attacks saturated hydrocarbons less readily than olefins. Consequently much higher concentrations of fluorine can be built up during reaction with saturated compounds so as to favor fluorination chains and diminish or prevent the formation of disproportionation and dimer-type products. For example, working in solution with saturated compounds Bockemüller[22] did not report evidence for the formation of condensed products although he did obtain such products from olefins. Substitution products were isolated from the reaction of fluorine with cyclohexane at Dry Ice temperature, *n*-hexadecane at 15°, *n*-butyric acid at 0°, and isobutyric acid at 15°.[23] In the same way, the high concentrations of oxygen and of chlorine present in the fluorine-sensitized reactions of pentachloroethane reported in this paper resulted almost exclusively in oxidation and in chlorination.

In order to understand the reactions of elemental fluorine, it is most important to differentiate between the reactivity of *fluorine molecules* and *fluorine atoms*. The very fact that explosive mixtures can be formed with fluorine and organic compounds points to appreciable activation energies for the reactions between molecular fluorine and the compounds involved.[24] However, even though the rate of reaction of molecular fluorine with an organic compound may be quite slow at a given temperature so as to permit mixing, by reaction fluorine atoms of exceedingly great reactivity[26] as well as free radicals are produced. With appreciable concentrations of both reactants present these can initiate highly exothermic reaction chains which may lead to uncontrolled reactions.

Reactions 1 and 2 provide a satisfactory basis for interpreting the reactions of fluorine with organic compounds observed at temperatures up to about 100°. At appreciably higher temperatures initiation by thermally produced fluorine atoms must also be considered. However, for thermal initiation to become an important mechanism, unreactive compounds are required; that is, compounds which are sufficiently stable to molecular fluorine to minimize reactions 1 and 2 at temperatures at which effective numbers of fluorine atoms are produced by thermal dissociation. Direct experimental evidence for such cases appears not to have been presented.[27]

**Mechanism of Radical Formation.**—Reactions 1 and 2 are regarded as *one electron displacements* on molecular fluorine by the $\pi$- and $\sigma$-electrons of carbon–carbon and carbon–hydrogen bonds.[28] They are made possible by the relatively low fluorine–fluorine and high carbon–fluorine and hydrogen–fluorine bond energies.[1] In general, reaction 1 occurs with great ease even at Dry Ice temperatures. Reaction 2 occurs less readily and shows a wide variation in rate dependent upon the electron availability at the reacting hydrogen. The accessibility and polarizability of the $\pi$-electrons of unsaturated linkages greatly facilitates reaction 1. These reactions between "even molecules," which produce free radicals by one-electron transfers, resemble reactions between "odd molecules" in that they do not involve charge separation and can take place in the vapor phase without solvated transition states as well as in the liquid phase.[20] The results now available suggest that elemental fluorine will prove to be an unusually versatile free radical initiator.

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in other important ways from those advanced speculatively by Bigelow, for example, as regards the formation of unsaturated and dimer-addition products.

[18] L. A. Bigelow, *Chem. Revs.*, **40**, 93 (1947).

[19] L. A. Bigelow, "Fluorine Chemistry," Ed., by J. H. Simons, Academic Press, Inc, New York, N. Y., 1950, Chap. 11, p. 387.

[20] Reference 18, p. 73.

[21] G. H. Cady, A. V. Grosse, L. L. Burger, E. J. Barber, Nat. Nuclear Energy Ser., I, VII, Ed. by C. Slesser and S. R. Schram, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, Chap. 34, pp. 719, 725.

[22] W. Bockemüller, *Ann.*, **506**, 20 (1933).

[23] Excess fluorine was reported to be present in the reactions with the butyric acids with which the most complete work was carried out. Only $\beta,\gamma$-substitution was shown to take place as would now be expected on the basis of a free radical mechanism by analogy with chlorination (see reference 18, p. 87). These results suggest that fluorine molecules, as well as fluorine atoms, attack preferentially the $\beta,\gamma$-positions of butyric acid. However, the conclusion that fluorine atoms react selectively with carbon–hydrogen bonds at 0° merits further investigation.

[24] Experimental results require a considerable range of values for reaction 2, for example, from low for $RH$[2,22] to high for $R_FH$[25]. Very low activation energies are generally indicated for reaction 1.[3,4] In contrast, the rate of initiation by fluorine atoms produced thermally would be expected to depend primarily upon temperature rather than type of compound.

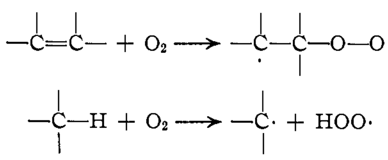
[25] O. Ruff and O. Bretschneider, *Ber.*, **69**, 303 (1936). The reaction of fluoroform with elemental fluorine was found to require ignition; mixtures were exploded by an electric spark. On the other hand, with highly reactive compounds, although burning may occur on mixing with fluorine if the high heat of reaction is not dissipated, it is impossible to prepare explosive mixtures.

[26] For example, the rate of reaction of fluorine atoms, produced by reaction 1, with the carbon hydrogen bond of chloroform appears to be diffusion controlled at Dry Ice temperature. Under the same conditions molecular fluorine shows very little, if any, reaction with chloroform.

[27] Thermally produced fluorine atoms may play an important role in the vapor phase fluorination of hydrocarbons with elemental fluorine at 200° to produce fluorocarbons. It was found that 200° was a preferred operating temperature while at 100° a high proportion of polymeric product was formed.[21] This observation may mean that with partially fluorinated hydrocarbons thermal initiation is important at 200° in preventing or minimizing intermittent locally uncontrolled reaction.

[28] This point of view is also preferred for the ionic reactions of the halogens in solution, *i.e.*, *two-electron displacements* on halogen molecules.

[29] Analogous one-electron displacements on the other halogens, as shown previously,[1] and on oxygen are indicated as energetically unfavorable for saturated hydrocarbons and simple olefins. However, it seems probable that a number of such processes occur which lead to resonance stabilized free radicals. For example, since this paper was submitted, kinetic measurements of the thermal reaction of oxygen with indene have been reported which are consistent with the occurrence of reactions i or ii at 50°.[30]



$$-\overset{|}{C}=\overset{|}{C}- + O_2 \longrightarrow -\underset{\cdot}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-O-O\cdot \qquad \text{(i)}$$

$$-\underset{|}{\overset{|}{C}}-H + O_2 \longrightarrow -\underset{|}{\overset{|}{C}}\cdot + HOO\cdot \qquad \text{(ii)}$$

[30] G. A. Russell, THIS JOURNAL, **78**, 1041 (1956); see also cited references to earlier work with Lienes.