Reactions of Fluorine Atoms

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I. Introduction

Although much has been written on the reactions and kinetics of chlorine, bromine, and iodine atoms, similar fluorine atom studies have been, up until a few years ago, minimal. This was due in part to the difficulty in producing a sufficient and measurable concentration of fluorine atoms free from molecular fluorine, and in part to the high reactivity of the atom. Consequently, reviews on halogen atom reactions, which are far from numerous to begin with, make little or no mention of fluorine atoms. Fettis and Knox[1] in a 1964 review of halogen atom reactions had only four references to fluorine atom kinetics. Although Wagner and Wolfrum[2] in their review of atom reactions included a short section on halogen atom reactions, references to fluorine atom chemistry are few. Warnatz and Zetzsch[3] mention several reactions of fluorine atoms studied by them prior to 1971. A list of a few rate constants for fluorine atom reactions was published in 1967 by Trotman-Dickenson and Milne,[4] but contained only six references. Somewhat more extensive is a 1966 list by Bahn,[5] but most entries pertain to rocket propulsion systems, and most of these are theoretical calculations.

In the past few years much interest in fluorine atom chemistry has been generated. This is in part due to the use of fluorine atoms in producing hydrogen fluoride lasers, and in part to the increase in the number of ways that atomic fluorine can be produced. Thus, the major advances in fluorine atom chemistry have been made over the last five years.

It is the purpose of this review to cover all work involving fluorine atom reactions of a so-called "macro kinetic" nature, stressing rate determination and reaction mechanism where available. Reactions of molecular fluorine are included wherever atomic fluorine plays an important role in the reaction scheme. We have decided, however, not to include work on fluorine-containing chemical lasers and the related field of "micro kinetics", i.e., studies of vibrational and rotational distributions. A bibliography of the greatest part of the HF chemical laser field up to 1973 appears in a paper by Arnold and Rojeska.[6] Our review will include only reports where chemical lasers were used to determine reaction rates or mechanisms.

II. Fluorine Atom Production, Detection, and Concentration Measurement

The earliest studies of fluorine atom kinetics relied on the thermal or photodissociation of molecular fluorine for the production of fluorine atoms.[7–13] With the exception of the work by Clark and Tedder,[11] who obtained absolute rate constants, the measurements were of relative rates only. Thermal dissociation of molecular fluorine produces an extremely low concentration of fluorine atoms in a high concentration of molecular fluorine. At room temperature, the concentration of fluorine atoms is of the order of 10^{-12} to 10^{-13} times the concentration of molecular fluorine. Emission at a wavelength of 365 nm has been used to produce fluorine atoms,[10,12] but as with thermal dissociation, a large concentration of molecular fluorine is present.

The existence of extremely reactive molecular fluorine unnecessarily complicates the reactions, and it is desirable to have a source of fluorine atoms free of molecular fluorine. Although early studies by Colebourne and co-workers[14] produced ^{18}F essentially free of F_2, extensive investigation of F atom reactions using F atoms free of molecular fluorine began with the work of Wagner and co-workers[15] in which they produced fluorine atoms by reaction of atomic nitrogen with NF_2 radicals generated by thermal dissociation of N_2F_4.

$$N + NF_2 \rightarrow 2F + N_2 \quad (1)$$

Despite disadvantages, such as low efficiency for production of atomic nitrogen from a microwave discharge with a resulting limit in the fluorine atom production, and the high cost of N_2F_4, a number of studies have been made using this method.[15–19]

Although studies in the early sixties of the ESR spectrum of atomic fluorine used radiofrequency[20,21] and microwave[22–24] discharges of dilute mixtures of F_2 in argon and CF_4 in argon as fluorine atom sources, these methods were not used as fluorine atom sources for kinetic studies until about 1971. McIntyre and McTaggart[25] produced fluorine atoms using a 28-MHz oscillator to discharge dry fluorine diluted 1:1000 with argon. Rosner and Allendorf[26] used an electrodeless microwave discharge to produce fluorine atoms from a gas mixture of 1% molecular fluorine and 99% argon at about 1 Torr in a dense alumina tube. Wagner, Warnatz, and Zetzsch[27] also described the production of fluorine atoms from a microwave discharge through a mixture of helium and a few parts per thousand of fluorine. Since 1971, a number of kinetic measurements have been made in which fluorine atoms were produced by this method, (e.g., ref 18, 28–32). The electrodeless microwave discharge has also been used to produce fluorine atoms from mixtures of CF_4 and helium[28,31,33,34] and from mixtures of SF_6 and helium.[35]

Kolb and Kaufman,[28] using a molecular beam analyzer,[36] studied the production of fluorine atoms in a microwave discharge through CF_4 and inert gas, and through mixtures of F_2 and argon. Using an alumina discharge section and a Teflon-coated flow tube, the only species present in quantity 30 cm downstream of the discharge through CF_4 were CF_4, C_2F_6, and atomic and molecular fluorine. No indication of CF, CF_3, or CF_2 radicals was found. Titration with hydrogen indicated an atomic fluorine concentration of $(0.4–1.0) \times 10^{-9}$ mol cm^{-3}, which was three to ten times the concentration of molecular fluorine. When they discharged mixtures of fluorine and argon, they found that for Ar:F_2 ratios between 5 and 20 at pressures of 0.5 to 1.5 Torr and linear flows of 50 to 100 cm s^{-1}, titration 30 cm downstream from the discharge indicated atomic fluorine concentrations of $(1–5) \times 10^{-9}$ mol cm^{-3}, but generally in the presence of two to five times as much molecular fluorine. Recently, Clyne and co-workers[18,31] have used a fast-flow discharge system with sampling by mass spectrometry to look at a number of fluorine atom reactions. A discharge through CF_4 (1%) and argon in a silica tube produced peaks for the CF^+, CF_2^+, CF_3^+ ions derived from the molecular species CF_4 and C_2F_6, and appreciable amounts of SiF_4 and O_2 from the interaction of the plasma with the silica walls of the discharge tube. In an attempt to remove any possibility of reactions with unrecombined molecular radicals formed from the discharge through CF_4, they examined the microwave discharge of mixtures of fluorine and helium. A clean silica discharge tube resulted in the production of fluorine atoms with SiF_4 as the only major impurity. The molecular fluorine was 80% dissociated when a 0.1% fluorine mixture was used, and at least 60% dissociated when a 1% fluorine mixture was used.

A normal electric discharge through NF_3[37] or SF_6[38] has also been used to produce fluorine atoms.

Fluorine atoms have been produced by the photolysis of a number of species. Berry[39] has compared a number of photolytic fluorine atom sources used by various workers for chemical laser studies including UF_6, XeF_4, SbF_5, MoF_6, N_2F_4, WF_6, CF_3I, $CF_2{=}CFCl$, and $CF_2{=}CFBr$. The use of N_2F_4 as a photolytic source of fluorine atoms has been extensively studied. Brus and Lin[40] have shown from mass spectrometric studies that emission below 210 nm will decompose N_2F_4 to give fluorine atoms. They also found that the NF_2 species, which is always in equilibrium with N_2F_4, will produce fluorine atoms when it absorbs radiation of about 250 nm. Bumgardner and Lawton[41] photolyzed N_2F_4 at 253 nm in the presence of alkanes and explained their results on the basis of extraction of hydrogen from the alkane by fluorine atoms, followed by reaction of the alkyl radical with NF_2 and N_2F_4. The flash photolysis of N_2F_4 has also been used to observe the radical FCO in the gas phase by reaction of F atoms with CO.[42] Fluorine atoms have also been produced by the reaction of molecular fluorine and nitric oxide

$$F_2 + NO \rightarrow NOF + F \qquad (2)$$

This method was used by Cool and Stephens[43] to produce the first continuous wave hydrogen fluoride chemical laser by the simple mixing of commercially available bottled gases. Recently Pollock and Jones[44] have used reaction 2 to produce fluorine atoms for kinetic studies.

Near-thermal ^{18}F atoms produced from the reaction $^{19}F(n,2n)^{18}F$ and moderated to near thermal energies through multiple collisions with SF_6 have also been used to study fluorine atom kinetics.[45]

Detection and concentration measurements of fluorine atoms have been achieved by mass spectrometry,[15,17,18,28,31,36,46,47] by electron paramagnetic resonance spectrometry,[20–24,48] by atomic resonance spectrometry,[30] by resistance monitoring of a hot filament,[26,29] and by monitoring emission from laser cavities.[37,49]

Because of the reactivity of molecular fluorine, attempts to find a chemical reaction that will allow a gas-phase titration have not been very successful. For example, the reactions

$$F + NOCl \rightarrow NO + FCl \qquad (3)$$

$$F + NO \xrightarrow{M} NOF + h\nu \qquad (4)$$

are complicated by the presence of molecular fluorine as in reaction 2 and by the possible reaction of molecular fluorine with NOCl.[26] Wagner and co-workers[15] have measured mass spectrometrically the yield of FCl formed in reaction 3 to obtain a measure of the fluorine atom concentration. They assumed no interference with molecular fluorine which was only a minor constituent in their system.

Kolb and Kaufman[28] carefully investigated the reaction of molecular hydrogen with fluorine atoms in the presence of molecular fluorine.

$$F + H_2 \rightarrow HF + H \qquad (5)$$

$$H + F_2 \rightarrow F + HF \qquad (6)$$

They showed by molecular beam analysis that molecular fluorine present in the system is titrated before atomic fluorine. Although the signal for atomic fluorine drops by a small fraction before all the molecular fluorine is consumed, they were able to determine the fluorine atom concentration from the difference in the hydrogen flows corresponding to removal of molecular fluorine and atomic fluorine.

Clyne and co-workers[31] have recently used the reaction with chlorine

$$F + Cl_2 \rightarrow FCl + Cl \qquad (7)$$

to determine the concentration of fluorine atoms by observing the Cl_2^+ mass peak. From earlier measurements, the reaction

$$Cl + F_2 \rightarrow FCl + F \qquad (8)$$

was found to be slow ($k_8^{298} \leq 3 \times 10^{10}$ cm^3 mol^{-1} s^{-1}) and was therefore not important relative to the fast reaction 7, $k_7^{298} = 5.4 \times 10^{13}$ cm^3 mol^{-1} s^{-1}. They further showed that no recombination of the chlorine atoms occurred within the sampling system. Ganguli and Kaufman[50] reported measurements of fluorine atom concentrations by titration with Cl_2 using the chlorine atom recombination emission as the endpoint indicator.

Recently, monitoring of the emission from reaction 4 has been used to determine rate constants for a number of reactions relative to the reaction of fluorine atoms with nitric oxide.[44]

III. Dissociation of Molecular Fluorine

A number of measurements of the rate constant for the

TABLE I. Rate Constants for Dissociation of Molecular Fluorine: $F_2 + M \rightarrow F + F + M$

Temp, K	k, $cm^3\ mol^{-1}\ s^{-1}$	M	Method	Ref
900–1900	$1.7 \times 10^{10} \exp(-14 \times 10^3/RT)$	Ar	Shock tube	*a*
1300–1600	$7.1 \times 10^{12} \exp[-(29.9 \pm 3.7) \times 10^3/RT]$	Ar	5% F_2 shock tube	55
1300–1600	$3.5 \times 10^{11} \exp[-(20.7 \pm 5.6) \times 10^3/RT]$	Ar	10% F_2 shock tube	55
1300–1600	$4.1 \times 10^{9} \exp[-(11.0 \pm 7.6) \times 10^3/RT]$	Ar	20% F_2 shock tube	55
1300–1600	$3.1 \times 10^{12} \exp[-(27.3 \pm 2.5) \times 10^3/RT]$	Ar	5% F_2 shock tube	*b*
1300–1600	$1.4 \times 10^{13} \exp(-31.1 \times 10^3/RT)$	20% Kr, 75% Ar	5% F_2 shock tube	*b*
1300–1600	$3.7 \times 10^{11} \exp(-19.6 \times 10^3/RT)$	20% Kr, 70% Ar	10% F_2 shock tube	*b*
1650–2700	$1.5 \times 10^{12} \exp(-23.9 \times 10^3/RT)$	Ne	Shock tube	*c*
1400–2000	$2.0 \times 10^{13} \exp(-35.0 \times 10^3/RT)$	Ne	Shock tube	138
1200–1500	$3.7 \times 10^{13} \exp(-31.7 \times 10^3/RT)$	Ar	Shock tube	*d*
1000–2000	$(4.5 \pm 2.4) \times 10^{12} \exp[-(28.5 \pm 2) \times 10^3/RT]$		Review	51
	$5 \times 10^{13} \exp(-35.1 \times 10^3/RT)$		(Estimate)	52
1400–2600	$3.59 \times 10^{13} \exp(-34.7 \times 10^3/RT)$	Ar	Shock tube	56
1400–2600	$9.85 \times 10^{13} \exp(-34.8 \times 10^3/RT)$	F_2	Shock tube	56

[a] R. L. Oglukian, Report AFRPL-TR-65-152, Air Force Rocket Propulsion Lab, 1965, as quoted in ref 52. [b] D. J. Seery and D. Britton, *J. Phys. Chem.*, 70, 4074 (1966). [c] R. W. Diesen, *J. Chem. Phys.*, **44**, 3662 (1966). [d] T. Just and G. Rimpel, Report DLR FB 70-02, Deutsche Luft und Raumfahrt, Munich, 1970, as quoted in ref 52.

TABLE II. Rate Constants for the Third-Order Recombination Reaction, $F + F + M \rightarrow F_2 + M$

Temp, K	k, $cm^6\ mol^{-2}\ s^{-1}$	M	Method	Ref
295	2.9×10^{13}	Ar	Microwave discharge F_2	50
295	$\sim 2.9 \times 10^{14}$	N_2	Microwave discharge F_2	50
	2.4×10^{14}	Ar	(Estimate)	58
	$1.275 \times 10^{14} T^{1/2}$		(Estimate)	59
	$\sim 10^{16}$	Ar	(Estimate)	46
	$1.1 \times 10^{18} T^{-1.5}$		(Estimate)	60
	$\sim 10^{15}$		(Estimate)	61
	$5.7 \times 10^{15} T^{-1}$	Ar	(Estimate)	62, *a*
	$5.7 \times 10^{15} T^{-1}$	F_2	(Estimate)	62, *a*
	$1.14 \times 10^{16} T^{-1}$	HF	(Estimate)	62, *a*
	$1.60 \times 10^{16} T^{-1}$	N_2	(Estimate)	62, *a*
	$2.28 \times 10^{16} T^{-1}$	F	(Estimate)	62, *a*
	$2.28 \times 10^{16} T^{-1}$	H_2O	(Estimate)	62, *a*
	$4.56 \times 10^{16} T^{-1}$	H_2	(Estimate)	62, *a*
	$7.41 \times 10^{16} T^{-1}$	O_2	(Estimate)	62, *a*
	$1.14 \times 10^{17} T^{-1}$	H	(Estimate)	62, *a*
	$2.28 \times 10^{16} T^{-1}$	O	(Estimate)	62, *a*
	$2.28 \times 10^{16} T^{-1}$	OH	(Estimate)	62, *a*
	$1.1 \times 10^{18} T^{-1.5}$	*b*	(Estimate)	62, *c*
1000–2000	$\sim 10^{14}$	Ar	(Estimate)	51
1000–2000	$3.1 \times 10^{11} \exp(8.33 \times 10^3/RT)$	Ar	(Estimate)	51
298	$\geqslant 3 \times 10^{15}$	Ar	Microwave discharge F_2	48

[a] R. C. Mitchell, Rocketdyne Report—R-7103 (AD828-742), 1968, as quoted in ref 62. [b] Representative "weighted" general third body. [c] S. S. Cherry, P. I. Gold, and L. J. Van Nice, TRW Systems Group 08832-6001-T000 (AD828-794), 1967, as quoted in ref 62.

thermal dissociation of molecular fluorine have been made by shock tube studies. These results are presented in Table I. A critical review of results to 1971 was presented by Lloyd.[51] The expression arrived at by Lloyd for the dissociation reaction

$$F_2 + M \rightarrow F + F + M \tag{9}$$

was $k_9 = (4.5 \pm 2.4) \times 10^{12} \exp[-(28.5 \pm 2) \times 10^3/RT]$ cm^3 mol^{-1} s^{-1}.

Assuming that the dissociation energy for molecular fluorine $[D^\circ_{298}(F_2)] = 38$ kcal mol^{-1}, Cohen,[52] in reports in 1971 and 1972, noted that any of the shock tube values lead to the strongly negative temperature dependence for fluorine atom recombination, resulting in unreasonably large values near 300 K. A very recent spectroscopic measurement[53] gives a value of $D_0(F_2) = 36.93$ kcal mol^{-1}. Cohen pointed out that the theoretical value of Shui, Appleton, and Keck[54] gives results which agree numerically with the shock tube study of Johnson and Britton,[55] but lead to an activation energy of 35.1 kcal mol^{-1} and a preexponential factor of $10^{13.7}$. Cohen thus suggested the value $k_9 = 5.0 \times 10^{13} \exp[-35.1 \times 10^3/RT]$ cm^3 mol^{-1} s^{-1} was acceptable. A very recent measurement of k_9 by Breshears and Bird[56] in which they made density gradient measurements in the shock tube by laser beam reflection, resulted in a value of $k_9 = 3.59 \times 10^{13} \exp(-34.7 \times 10^3/RT)$ cm^3 mol^{-1} s^{-1} in the presence of argon.

IV. Recombination and Wall Reactions

A. Recombination Reactions

Although the recombination reactions of the other halogens have been studied quite extensively, there has been relatively little work done on the recombination of fluorine atoms, and most of this has been theoretical. Lloyd[51] has published a critical review on the dissociation and recombination reactions of chlorine and fluorine, but was only able to discuss the fluorine recombination briefly. Using the methods of Benson and Fueno,[57] Lloyd arrived at an average value of 10^{14} cm^6 mol^{-2} s^{-1} for the rate constant for the reaction

$$F + F + M \rightarrow F_2 + M \tag{10}$$

where M = Ar. Using the rate constant for dissociation and the equilibrium constant, Lloyd estimated k_{10} at $3.1 \times 10^{11} \exp(4190/T)$ cm^6 mol^{-2} s^{-1}, but argued that the temperature dependence was probably too large. Other theoretical estimates

TABLE III. Wall-Catalyzed Fluorine Atom Reactions

k, s^{-1}	System	Reactants present	Ref
	$\frac{1}{2}F \xrightarrow{\text{wall}} F_2$		
2.3–2.5	Teflon	F atoms	50
10	Quartz–alumina	F atoms	48
	$\frac{1}{2}F \xrightarrow{\text{wall}}$ products		
11.9	Pyrex	$F + NO + CH_3F$	44
15	Pyrex	$F + NO + CH_2F_2$	44
2.5	Pyrex	$F + NO + CHF_3$	44
29.9	Pyrex	$F + NO + CHClF_2$	44
4.9	Pyrex	$F + NO + HCl$	44
23.1	Pyrex	$F + NO + CBrF_3$	44
53.8	Pyrex	$F + NO + NH_3$	44

of k_{10}[46,58-61] place the figure in the range of 10^{14}–10^{16} cm^6 mol^{-2} s^{-1}. These estimates appear in Table II, together with a list of relative values for k_{10} with various M, compiled by Bahn et al.[62]

Only two experimental reports on the recombination reaction are known to date. Valance et al.[48] used ESR line strengths as a measure of F atom concentration to study the recombination reactions in a quartz–alumina flow tube. An approximate rate constant $k_{10} \geq 3 \times 10^{15}$ cm^6 mol^{-2} s^{-1} was in good agreement with the theoretical results. Ganguli and Kaufman[50] obtained a value for k_{10} with M = Ar of 2.9×10^{13} cm^6 mol^{-2} s^{-1}, about one to two orders of magnitude lower than the other results. Experiments using N_2 as a third body showed it to be ten times more efficient than argon. This was explained by the weak F_2–Ar attraction.

B. Wall Reactions

The first-order wall-catalyzed recombination of F atoms

$$F \xrightarrow{\text{wall}} \tfrac{1}{2}F_2 \tag{11}$$

has not in itself been the subject of any studies, but values for the rate constant under various conditions have evolved during the studies of other F atom reactions. The wall reaction was considered by Ganguli and Kaufman[50] and Valance et al.,[48] in their recombination studies. Pollock and Jones[44] reported rate constant values for the general wall-catalyzed removal of F atoms during comparative reactions between F + NO and F + other reactants. The reported rate constants appear in Table III.

V. Reaction with H_2, D_2, HD, and H

The reaction of fluorine atoms with hydrogen is probably the most extensively studied of any F atom reaction. The process involves the abstraction of a hydrogen atom.

$$F + H_2 \rightarrow HF + H \tag{12}$$

The reaction, which is exothermic by about 32 kcal mol^{-1}, allows vibrational population up to the $v = 3$ level of HF. This reaction was utilized by Deutsch[63] and by Kompa and Pimentel[64] to supply the chemical pumping for an HF chemical laser. The HF chemical laser is included in a review by Arnold and Rojeska.[6]

Eyring and Kassel[65] predicted "little or no activation energy" for the reaction of F atoms with hydrogen. They attributed the exothermicity of the $F_2 + H_2$ reaction solely to the decomposition of F_2. For this reason, they stated that fluorine and hydrogen will not react at liquid hydrogen temperatures without a catalyst. Glasstone, Laidler, and Eyring[66] later estimated the activation energy, based on a semiempirical method, to be between 6.3 and 10.6 kcal mol^{-1}. Hirschfelder[67] showed that the activation energy was a function only of the binding energy, and not of atomic size or the diatomic force constant.

Reaction 12 is discussed briefly in a review by Wagner and Wolfrum,[2] and a partial list of theoretical and experimental rate constants appears in papers by Bahn[5] and Cohen.[52]

Levy and Copeland[68] studied the F_2/H_2 reaction at 383 K in a flow system. Iodometry was used to determine the molecular fluorine concentration. The reaction rate was found to be proportional to the F_2 concentration and independent of both the H_2 concentration and the surface area to volume ratio. Brokaw[69] was able to explain the data by a mechanism which involved an energy transfer chain-branching step.

$$F + H_2 \rightarrow HF + H \tag{12}$$

$$HF + F_2 \rightarrow \alpha HF^* + (1 - \alpha)HF + 2F \tag{13}$$

$$HF^* + F_2 \rightarrow HF + 2F \tag{14}$$

$$HF^* + M \rightarrow HF + M \tag{15}$$

$$2F + M \rightarrow F_2 + M \tag{10}$$

or

$$2F + H_2 \rightarrow 2HF \tag{16}$$

Rabideau et al.[70] did not find steps 15 or 16 to be important chain termination steps, but included the following steps:

$$H + H + M \rightarrow H_2 + M \tag{17}$$

$$F + H + M \rightarrow HF + M \tag{18}$$

Attempts to find a definite value for the chain branching step 14 were unsuccessful. Results for k_{14} were inconsistent, indicating that the wall reaction varied in importance.

Burwell et al.[59] studied the mechanism for the F_2/H_2 rocket propulsion system and listed reactions 17 and 18 to be the rate-controlling steps.

Much of the work on $F + H_2$ has been the determination of relative rate constants. Mercer and Pritchard[7] reacted fluorine with H_2/CH_4 mixtures both thermally and photochemically in both metal and quartz reaction vessels. The amounts of products formed were measured mass spectrometrically. The relative rate constants were found to be independent of the concentration of F_2, H_2, CH_4, inert carrier gas, or the type of reaction vessel used. The value of k_{19}/k_{12} where k_{19} is the rate constant for

$$F + CH_4 \rightarrow HF + CH_3 \tag{19}$$

was reported to be $1.05 \exp[(0.5 \pm 0.2) \times 10^3/RT]$. Kapralova et al.,[71] using ESR to determine products, found a value of 0.935 kcal for the differences in activation energy ($E_{12} - E_{19}$) as opposed to Mercer and Pritchard's value of 0.5 kcal.[7] Kapralova et al.[71] suggested that in the earlier work the greater concentration of F_2 in the mixture resulted in more highly fluorinated methanes than the monofluoride which gave too small a value for $E_{12} - E_{19}$. Values of the ratio k_{12}/k_{19} were also found by Foon and Reid[72] and by Jonathan et al.[33] The latter utilized the infrared chemiluminescence technique to measure relative rates as a function of relative intensities of some strong HF transition lines.

The isotope effect on the ratio k_{F+H_2}/k_{F+D_2} has been studied experimentally by reaction of mixtures of F and F_2 with H_2/D_2 mixtures. The relative yields of HF and DF were determined by passing the products through a high-frequency discharge and measuring by ESR the concentrations of H and D formed.[71] This ratio was also determined by direct measurement of products using a mass spectrometer,[73] by chromatography,[74] and by a modified nuclear hot atom technique.[75] The relative rates have also been determined theoretically by Jaffe and Anderson[76] and Muckerman[77] using classical trajectory analysis. In most reports, the activation energy difference $E_{F+H_2} - E_{F+D_2}$ is found to be nearly negligible. Kapralova et al.[71] explained this by saying that since the activation energies themselves are small, there is no necessity for the formation of an intermediate complex having a configuration corresponding to a minimal activation energy. Foon et al.[74] allowed that while this may be true for cases where the activation energy is truly zero, it did not hold in this case where the activation energies were small, but finite.

The rate constant of the reaction of F atoms with molecular hydrogen has also been found relative to F atom reactions with ethane[72] and acetylene.[45]

$$F + C_2H_6 \rightarrow HF + C_2H_5 \qquad (20)$$

$$F + HC{\equiv}CH \rightarrow HFC{=}CH \qquad (21)$$

In addition, the rate constant of the reaction of F atoms with molecular deuterium has been found relative to reaction 19,[71,74] reaction 20,[74] and to reaction 21.[45]

Williams and Rowland[45,78] produced nearly thermal ^{18}F atoms by neutron bombardment of ^{19}F atoms in an excess of SF_6, and used these to study competitively the reactions

$$F + RH \rightarrow HF + R \qquad (22)$$

where R = H, CH_3, C_2H_5, C_2H_3, Cl, Br, I, CH_2CF_3, and HS.

Persky[35] studied the isotope effect between the reactions

$$F + HD \rightarrow FH + D \qquad (23)$$

$$F + DH \rightarrow FD + H \qquad (24)$$

using a quadrupole mass spectrometer to determine the ratio of the concentrations of HF and DF. The ratio k_{23}/k_{24} was found to be $(1.26 \pm 0.02) \exp[-(70 \pm 6)/RT]$. Berry[79] obtained a value of 1.42 ± 0.1 for the same ratio from a chemical laser measurement.

Recently, Klein and Persky[80] reported the relative rates for the reaction of fluorine atoms with para and ortho hydrogen to be unity at 237 and 298 K and 1.05 ± 0.02 at 175 K.

A complete summary of the rates of reaction of fluorine atoms with H_2, D_2, and HD relative to the rates of reaction of fluorine atoms with other compounds is given in Table IV.

The first absolute rate constant found experimentally for the $F + H_2$ reaction, $k_{12} = 10^{14.2} \exp(-1.6 \times 10^3/RT)$ cm^3 mol^{-1} s^{-1}, was reported by Homann et al.[15] Reaction of active nitrogen with NF_2 was used to produce fluorine atoms, while their concentration was determined by reaction with NOCl.

Dodonov et al.[81] used a mass spectrometer to determine rate constants for the reaction of F atoms with H_2 by following both the rate of disappearance of H_2 molecules and the rate of appearance of H atoms. The results from the two determinations were then averaged to give a rate constant $k_{12}{}^{293} = 1.6 \times 10^{13}$ cm^3 mol^{-1} s^{-1}.

Foon and Reid[72] reported a value of $4.85 \times 10^{13} \exp(-2.47 \times 10^3/RT)$ cm^3 mol^{-1} s^{-1} for the rate constant, based on their comparative studies with the reactions of F atoms with CH_4 and C_2H_6, coupled with the absolute rate constant for the $F + CH_4$ reaction derived by Fettis et al.[9]

Homann and MacLean[82] and MacLean[83] measured mass spectrometrically the concentration of reactants, intermediates, and products formed in H_2–F_2 flames and found $k_{12}{}^{2000\,K} = 0.9 \times 10^{14}$ cm^3 mol^{-1} s^{-1}.

Kompa and Wanner[49] produced F atoms by flash photolysis of WF_6. From the intensity of the HF laser emission produced, a value of $k_{12} = 3.8 \times 10^{13}$ cm^3 mol^{-1} s^{-1} was determined.

Rabideau et al.[70] gave $k_{12} = 4 \times 10^{12}$ cm^3 mol^{-1} s^{-1}, which was an order of magnitude smaller than the value found in most of the other studies. They produced F atoms by the reaction of molecular fluorine with atomic hydrogen and followed the concentrations of F and H by ESR. The only other experimental result which gave so small a rate constant was that reported by Lam et al.,[84] using a laser cavity containing NF_3 and H_2. Igoshin et al.[37,85] measured k_{12} as a function of hydrogen pressure and energy of initiating pulse. They found that k_{12} increased with initiation energy and decreased with increasing H_2 concentration. Their value, $9.28 \times 10^{13} \exp[-(1.08 \pm 0.17) \times 10^3/RT]$ cm^3 mol^{-1} s^{-1}, for k_{12} agreed with that found in the majority of experiments.

Clyne and co-workers[31] arrived at a value of 1.5×10^{13} cm^3 mol^{-1} s^{-1} for k_{12}, using mass spectrometric analysis, and the F + ClNO reaction as a measure of F concentration. The authors admitted to a great deal of scatter in their measurements and reported a 50% error range.

A number of theoretical calculations have also been reported for the H_2/F_2 system leading to estimates of the rate constants for reaction 12. Wilde[86] treated the system as analogous to O + H_2, while Burwell et al.[59] used as a comparison the reactions of other halogen atoms with hydrogen. Bittker[87] used values obtained by Jacobs et al.[88] for k_{-25}

$$F + H_2 \rightleftarrows H + HF \qquad (25)$$

together with the equilibrium constant, in order to obtain values for k_{25} between 2000 and 5000 K. Other values were obtained using activated complex theory,[89,90] classical trajectory analysis,[76] near-equilibrium criteria,[91] and phase space trajectory theory.[92] The value for k_{12} obtained by Jaffe[92] is somewhat smaller than previous values, which he attributes to the assumption of too large a barrier on the potential surface.

Levy and Copeland[93] in their studies of the $H_2/O_2/F_2$ system estimated an activation energy of 5.7 kcal mol^{-1} for reaction 12. From activation energy differences between the reactions $F + H_2$ and $F + CH_4$, and the results of Fettis et al.,[9] for the reaction $F + CH_4$, Kapralova et al.[71] arrived at an activation energy of 2.145 ± 0.23 kcal mol^{-1} for the $F + H_2$ reaction. Otozai[94] assumed that the bond distance in an activated complex is equal to the bond distance corresponding to the inflection point on the potential energy curve of the pair of atoms and calculated an activation energy of 10.4 kcal mol^{-1} for reaction 12. Ellison and Patel[95] considered the three atom system to be represented by a resonance of the two canonical structures F H–H and F–H H and calculated a value for the activation energy of 5 kcal mol^{-1}. Johnston and Parr[96] used bond energy considerations to estimate the activation energy for reaction 12 as 2 kcal mol^{-1}. Chakraborty and Pan[97] arrived at a value of 2.13 kcal mol^{-1} from a modified London–Eyring–Polanyi–Sato calculation.

Levy and Copeland[93] studied the effect of oxygen on the thermal reaction between F_2 and H_2. The system was studied by measuring the rate of disappearance of F_2 from its absorption at 284.9 nm. It was found that the reaction was inhibited by oxygen. The inhibition was suggested to be caused by the following steps

$$H + O_2 + M \rightarrow HO_2 + M \qquad (26)$$

$$F + O_2 + M \rightarrow FO_2 + M \qquad (27)$$

Brokaw[98] explained the results of Levy and Copeland[93] by the following mechanism:

$$F + H_2 \rightarrow HF + H \qquad (12)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (26)$$

$$HO_2 + F_2 \rightarrow HF + O_2 + F \qquad (28)$$

$$F + HO_2 \rightarrow HF + O_2 \qquad (29)$$

$$H + O_2 \rightarrow OH + O \qquad (30)$$

$$O + H_2 \rightarrow OH + H \qquad (31)$$

$$OH + H_2 \rightarrow H_2O + H \qquad (32)$$

$$F_2 + H_2O \xrightarrow{\text{wall}} 2HF + \tfrac{1}{2}O_2 \qquad (33)$$

It was suggested that, with small amounts of oxygen present, reaction 34 competes with reaction 26, but at high oxygen concentrations, reaction 34 is overwhelmed. An overall rate constant for the reaction was given by $k = k_{12}k_{30}k_{28}/k_{26}k_{29}$.

TABLE IV. Relative Rates of Reaction with H_2, D_2, and HD

Temp, K	k_1/k_2	$E_1 - E_2$, kcal mol^{-1}	Method	Ref
(1) $F + H_2 \rightarrow FH + H$; (2) $F + CH_4 \rightarrow FH + CH_3$				
298–432	$0.95 \exp[-(500 \pm 200)/RT]$	0.5 ± 0.2	Thermal and photochemical reaction, $F_2 + H_2/CH_4$	7
77–353	$0.41 \exp[-935/RT]$[a]	0.935	Thermal reaction, $F_2 + H_2/D_2/CH_4$	71
253–348	$1.22 \pm 0.005 \exp[-(630 \pm 300)/RT]$	0.630 ± 0.3	Reaction $F_2 + H_2/CH_4$	72
300	0.74 ± 0.07		Microwave discharge CF_4	33
283	0.33[a]		Neutron bombardment	45
283	0.34[a]		Neutron bombardment	78
300	0.38		Electrical discharge SF_6	84
(1) $F + H_2 \rightarrow FH + H$: (2) $F + C_2H_6 \rightarrow FH + C_2H_5$				
273–343	$4.6 \pm 2.1 \exp[-(1{,}950 \pm 270)/RT]$	1.95	Reaction $F_2 + H_2/C_2H_6$	72
283	0.12[a]		Neutron bombardment	45
283	0.10[a]		Neutron bombardment	78
300	0.17		Electrical discharge SF_6	84
(1) $F + H_2 \rightarrow FH + H$; (2) $F + C_3H_8 \rightarrow FH + C_3H_7$				
300	0.083		Electrical discharge SF_6	84
(1) $F + H_2 \rightarrow FH + H$; (2) $F + n\text{-}C_4H_{10} \rightarrow FH + n\text{-}C_4H_9$				
300	0.05		Electrical discharge SF_6	84
(1) $F + H_2 \rightarrow FH + H$; (2) $F + i\text{-}C_4H_{10} \rightarrow FH + i\text{-}C_4H_9$				
300	0.05		Electrical discharge SF_6	84
(1) $F + H_2 \rightarrow FH + H$; (2) $F + CH_3CF_3 \rightarrow FH + H_2CCF_3$				
283	2.80[a]		Neutron bombardment	45
283	2.64[a]		Neutron bombardment	78
(1) $F + H_2 \rightarrow FH + H$: (2) $F + HC{\equiv}CH \rightarrow FH + C{\equiv}CH$				
283	1.17[a]		Neutron bombardment	45
283	1.00[a]		Neutron bombardment	78
(1) $F + H_2 \rightarrow FH + H$: (2) $F + HCl \rightarrow FH + Cl$				
300	3.89[a]		Microwave discharge CF_4	33
(1) $F + H_2 \rightarrow FH + H$; (2) $F + HBr \rightarrow FH + Br$				
300	0.85[a]		Microwave discharge CF_4	33
(1) $F + H_2 \rightarrow FH + H$; (2) $F + HI \rightarrow FH + I$				
300	0.62[a]		Microwave discharge CF_4	33
283	0.35[a]		Neutron bombardment	45
283	0.38[a]		Neutron bombardment	78
(1) $F + H_2 \rightarrow FH + H$: (2) $F + H_2S \rightarrow FH + SH$				
283	0.11[a]		Neutron bombardment	78
(1) $F + H_2 \rightarrow FH + H$; (2) $F + D_2 \rightarrow FD + D$				
77–293	$1.48 \pm 0.22 \exp[+(45 \pm 30)/RT]$	−0.045	Thermal reaction. $F_2 + H_2/D_2$	71
163–417	$1.04 \pm 0.02 \exp[+(370 \pm 100)/RT]$	−0.370	Microwave discharge SF_6 or CF_4	73
273–348	$1.5 \pm 0.4 \exp[+(130 \pm 300)/RT]$	−0.130	Derived from $F + H_2/CH_4$ and $F + D_2/CH_4$	74
283	1.8[a]		Neutron bombardment	45, 78
300–1000	$1.64 \exp[+1610/RT]$	−1.61	(Estimate)	76
303–475	$1.11 \pm 0.05 \exp[+(356 \pm 26)/RT]$	−0.356	Neutron bombardment	75
300	1.41		(Estimate)	77
(1) $F + H_2 \rightarrow FH + H$; (2) $F + HD \rightarrow FH + D$				
297	2.63 ± 0.21		Photochemical decomposition CF_3I	79
(1) $F + H_2 \rightarrow FH + H$: (2) $F + CD_4 \rightarrow FD + CD_3$				
283	0.52[a]		Neutron bombardment	45
283	0.58[a]		Neutron bombardment	78
(1) $F + H_2 \rightarrow FH + H$: (2) $F + HC{\equiv}CH \rightarrow HFC{=}CH$				
283	0.14		Neutron bombardment	45
(1) $F + D_2 \rightarrow FD + D$: (2) $F + CH_4 \rightarrow FH + CH_3$				
223–353	$0.28 \exp[-(980 \pm 150)/RT]$	0.980	Thermal reaction $F_2 + D_2/CH_4$	71
183–348	$0.79 \exp[-(719 \pm 23)/RT]$	0.719	Reaction $F_2 + D_2/CH_4$	74
283	0.19[a]		Neutron bombardment	45
283	0.20[a]		Neutron bombardment	78
(1) $F + D_2 \rightarrow FD + D$; (2) $F + C_2H_6 \rightarrow FH + C_2H_5$				
273–346	$3.70 \exp[-(2120 \pm 210)/RT]$	2.120	Reaction $F_2 + D_2/C_2H_6$	74
283	0.07[a]		Neutron bombardment	45
283	0.06[a]		Neutron bombardment	78
(1) $F + D_2 \rightarrow FD + D$: (2) $F + CH_3CF_3 \rightarrow FH + H_2CCF_3$				
283	1.60[a]		Neutron bombardment	45
283	1.51[a]		Neutron bombardment	78

TABLE IV (Continued)

Temp, K	k_1/k_2	$E_1 - E_2$, kcal mol^{-1}	Method	Ref
	(1) $F + D_2 \rightarrow FD + D$; (2) $F + HC{\equiv}CH \rightarrow FH + C{\equiv}CH$			
283	0.67[a]		Neutron bombardment	45
283	0.57[a]		Neutron bombardment	78
	(1) $F + D_2 \rightarrow FD + D$; (2) $F + HI \rightarrow FH + I$			
283	0.20[a]		Neutron bombardment	45
283	0.22[a]		Neutron bombardment	78
	(1) $F + D_2 \rightarrow FD + D$; (2) $F + H_2S \rightarrow FH + SH$			
283	0.06[a]		Neutron bombardment	78
	(1) $F + D_2 \rightarrow FD + D$; (2) $F + CD_4 \rightarrow FD + CD_3$			
283	0.30[a]		Neutron bombardment	45
283	0.33[a]		Neutron bombardment	78
	(1) $F + D_2 \rightarrow FD + D$; (2) $F + HC{\equiv}CH \rightarrow HFC{=}CH$			
283	0.08		Neutron bombardment	45
	(1) $F + D_2 \rightarrow DF + D$; (2) $F + DH \rightarrow DF + H$			
297	2.08 ± 0.13		Photochemical decomposition, CF_3I	79
	(1) $F + HD \rightarrow FH + D$: (2) $F + DH \rightarrow FD + H$			
159–413	$1.26 \pm 0.02 \exp[+(70 \pm 6)/RT]$	−0.70	Microwave discharge, SF_6	35
297	1.42 ± 0.1		Photochemical decomposition CF_3I	79
300	1.18		(Estimate)	77
	(1) $F + p\text{-}H_2 \rightarrow FH + H$; (2) $F + o\text{-}H_2 \rightarrow FH + H$			
237, 298	1.00 ± 0.02		Microwave discharge SF_6	80
175	1.05 ± 0.02		Microwave discharge SF_6	80

[a] These results, although not presented in the original reference, have been calculated from other ratios given in the reference.

TABLE V. Summary of the Published Arrhenius Parameters for H_2 and D_2

Temp, K	E, kcal mol^{-1}	Log A, cm^3 mol^{-1} s^{-1}	Method	Ref
		$F + H_2 \rightarrow H + HF$		
293	$k = (1.8 \pm 0.6) \times 10^{13}$		High frequency discharge F_2/He	81
~300	$k = 3.8 \times 10^{13}$		Flash photolysis WF_6, HF chemical laser	49
300–400	1.6	14.2	$N + NF_2$	15
293	$k = (4 \pm 1) \times 10^{12}$		Reaction $H + F_2$	70
195–296	1.08 ± 0.17	13.97	Electrical discharge NF_3	37
253–348	2.47 ± 0.03	13.66–13.71	Comparison	72
~2000	$k = 0.9 \times 10^{14}$		H_2/F_2 flame	82, 83
	5.7	12.7	(Estimate)	86, *a–c*
	$k = 2.454 \times 10^{10} T \exp(-8.001 \times 10^3/RT)$		(Estimate)	59
1000–4000	$k = 7.8 \times 10^{11} T^{0.69} \exp(-2.5 \times 10^3/RT)$		(Estimate)	89
300–1000	2.34	14.1	(Estimate)	76
300	$k = 1.4 \times 10^{12}$		Electrical discharge SF_6, HF chemical laser	84
	6.3 – 10.6		(Estimate)	66
>3640	$k > 3 \times 10^{13}$		(Estimate)	91
	10.4		(Estimate)	94
	5		(Estimate)	95
298–2500	$k = 1.2 \times 10^{12} T^{0.67} \exp(-2.6 \times 10^3 RT)$		(Estimate)	90
300	$k = 0.64 \times 10^{12}$		(Estimate)	92
395–435	5–7		Reaction $F_2 + O_2 + H_2$	93
77–353	2.145 ± 0.23		Reaction $F_2 + H_2/D_2/CH_4$	71
2000–5000	$k = 2.04 \times 10^{13} T^{-0.12} \exp(-3.75 \times 10^3/RT)$		(Estimate)	87
298	$k = (1.5 \pm 50\%) \times 10^{13}$		Microwave discharge CF_4	31
	2		(Estimate)	96
	2.13		(Estimate)	97
	$k = 2.45 \times 10^{10} T \exp(-8 \times 10^3/RT)$		(Estimate)	*d*
250–500	1.6	14.13	(Estimate)	*e*
		$F + D_2 \rightarrow D + DF$		
195–296	0.79 ± 0.18	13.69	Electrical discharge NF_3	37
300–1000	2.16	13.8	(Estimate)	76'
223–353	2.75		Reaction $F_2 + D_2/CH_4$	71
183–348	2.60	13.48	Reaction $F_2 + D_2/CH_4$, C_2H_6	74

[a] S. W. Mayer, E. A. Cook, and L. Schieler, Aerospace Corp. Report, TDR·269(4210·10)-6, 1964, as quoted in ref 5. [b] E. A. Cook and L. Schieler, Aerospace Corp. Report TDR·269(9210·02)·1, 1964, as quoted in ref 5. [c] P. I. Gold, TRW Systems Report 5435·6005-TU000, 1965, as quoted in ref 5. [d] W. G. Burwell, V. J. Sarli, and T. F. Zupnik, United Aircraft Corp. 3rd Conference on Performance of High Temperature Systems, 1964, as quoted in ref 5. [e] R. Wilkins, Aerospace Corp. Report TR·0059 (6753·20)·1, 1971, as quoted in ref 52.

TABLE VI. Summary of the Published Rate Constants for F + H + M → FH + M

Temp, K	M	k, cm^6 mol^{-2} s^{-1}	Method	Ref
	Ar	$2.5 \times 10^{18}T^{-1}$	(Estimate)	62, *a*, *b*
	F_2	$2.5 \times 10^{18}T^{-1}$	(Estimate)	62, *a*
	HF	$5.0 \times 10^{18}T^{-1}$	(Estimate)	62, *a*
	N_2	$7.0 \times 10^{18}T^{-1}$	(Estimate)	62, *a*
	F	$1.0 \times 10^{19}T^{-1}$	(Estimate)	62, *a*
	H_2O	$1.0 \times 10^{19}T^{-1}$	(Estimate)	62, *a*
	H_2	$2.0 \times 10^{19}T^{-1}$	(Estimate)	62, *a*
	O_2	$3.25 \times 10^{19}T^{-1}$	(Estimate)	62, *a*
	H	$5.0 \times 10^{19}T^{-1}$	(Estimate)	62, *a*
	O	$1.0 \times 10^{20}T^{-1}$	(Estimate)	62, *a*
	OH	$1.0 \times 10^{20}T^{-1}$	(Estimate)	62, *a*
	M[c]	$7.5 \times 10^{18}T^{-1}$	(Estimate)	62, *d*
		$7.5 \times 10^{18}T^{-1}$	(Estimate)	86, 87
	Ar	4.912×10^{15} $\exp(3.05 \times 10^3/RT)$	(Estimate)	59
2000–5000	Ar	$3.0 \times 10^{18}T^{-1}$	(Estimate)	87
2000–5000	HF	$3.0 \times 10^{19}T^{-1}$	(Estimate)	87
		$10^{18}T^{1/2}$	(Estimate)	*e*
		$1.09 \times 10^{15}T^{1/2}$	(Estimate)	*f*
	HF	$10^{19}T^{-1/2}$	(Estimate)	*g*
	H_2	$7 \times 10^{17}T^{-1/2}$	(Estimate)	*g*
	H	$3.5 \times 10^{17}T^{-1/2}$	(Estimate)	*g*
	H_2O	$10^{19}T^{-1/2}$	(Estimate)	*g*
	H_2O	$5 \times 10^{18}T^{-1/2}$	(Estimate)	*h*
	OH	$10^{19}T^{-1/2}$	(Estimate)	*g*
	OH	$5 \times 10^{18}T^{-1/2}$	(Estimate)	*h*
1000–3500		$3.6 \times 10^{19}T^{-1}$	(Estimate)	*b*
		$7.2 \times 10^{18}T^{-1}$	(Estimate)	*b*

[a] R. C. Mitchell, Rocketdyne Report, R-7103(AD828·742), 1968. [b] D. Garvin, National Bureau of Standards Report 9884, 1968. [c] Representative "weighted" general third body. [d] S. S. Cherry, P. I. Gold, and L. J. Van Nice, TRW Systems Group 08832·6001·T000 AD 828-794, 1968. [e] C. T. Crowe, R. Dunlap, R. W. Hermsen, M. Rogers, P. G. Willoughby, H. Wolff, and R. Woolfolk, United Technical Center Report UTC, 2128·FR, 1966, as quoted in ref 5. [f] W. G. Burwell, V. J. Sarli and T. F. Zupnik, United Aircraft Corp. 3rd Conference on Performance of High Temperature Systems, 1964, as quoted in ref 5. [g] S. W. Mayer, E. A. Cook, and L. Schieler, Aerospace Corp. Report TDR·269 (4210·10)-6, 1964, as quoted in ref 5. [h] R. Tunder, S. W. Mayer, and L. Schieler, Aerospace Corp. Report TDR·1001 (9210·02)-1, 1966, as quoted in ref 5.

$$H + F_2 \rightarrow HF + F \qquad (34)$$

Vedeneev et al.[99] showed by ESR studies that, during the reaction of F_2 with H_2 in the presence of O_2, there was a buildup of HO_2 but not of FO_2 indicating that reaction 26 was much faster than reaction 27.

Following photolytic dissociation of F_2 by 313 nm radiation, Levy and Copeland[100] proposed the following mechanism for the oxygen-inhibited reaction between H_2 and F_2.

$$F + H_2 \rightarrow HF + H \qquad (12)$$

$$H + F_2 \rightarrow HF + F \qquad (34)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (26)$$

$$HO_2 + F_2 \rightarrow HF + O_2 + F \qquad (28)$$

$$F + HO_2 \rightarrow HF + O_2 \qquad (29)$$

Although the following steps were deemed possible

$$F + O_2 + M \rightarrow FO_2 + M \qquad (27)$$

$$FO_2 + H_2 \rightarrow HF + O_2 + H \qquad (35)$$

they were not considered to play an important role in the inhibition of the reaction. Step 26 was considered the likely source of inhibition since HO_2 is much less reactive than FO_2.

Absolute rate constants for the reaction of F atoms with deuterium have been reported by Igoshin et al.[37] and by Foon et al.[74] In addition, Jaffe and Anderson[76] calculated a value for the rate constant based on a classical trajectory analysis. The values for the preexponential constant in all cases are between 13.5 and 14 cm^3 mol^{-1} s^{-1}, but the value of Igoshin et al. for the activation energy is about one-third the other values. Kapralova et al.[71] reported an activation energy of 2.75 kcal, which is in good agreement with the majority of other values.

A complete summary of values of the Arrhenius parameters determined for the reactions of fluorine atoms with molecular hydrogen and molecular deuterium are presented in Table V.

The termolecular recombination reaction

$$F + H + M \rightarrow HF + M \qquad (18)$$

has been studied for a variety of third bodies. The process has been found to be important and, in fact, rate controlling in F_2/H_2 rocket propulsion systems.[59] Bittker[87] has studied the system for M = Ar and HF. His value for M = Ar of $3.0 \times 10^{18}/T$ cm^6 mol^{-2} s^{-1} was based upon the results obtained by Jacobs et al.[88] for the bimolecular decomposition of HF in a shock tube. The values for M = HF, the situation actually occurring in a rocket nozzle, were based on the assumption that HF should be ten times as efficient a third body as argon. Bahn et al.[62] has compiled a list of "recommended recombination rate constants" for reaction 18 for eleven different third bodies, and also reported a value of $k_{18} = 7.5 \times 10^{18}/T$ cm^6 mol^{-2} s^{-1} for a representative "weighted" general third body. The rate constants for reaction 18 are listed in Table VI.

VI. Reaction with Halogen-Containing Compounds

A. Reaction with Hydrogen Fluoride

A direct experimental study of the exchange reaction

$$F + HF \rightarrow FH + F \qquad (36)$$

has not yet been made. Solomon et al.,[101] during studies on vibrationally excited HF, concluded that in the F + HF reaction vibrationally excited HF is produced by H atom abstraction. Mayer

TABLE VII. Reaction with Halogen-Containing Compounds

Temp, K	E, kcal mol^{-1}	k, cm^3 mol^{-1} s^{-1}	Method	Ref
		$F + HF \rightarrow FH + F$		
298–2500		$3.5 \times 10^{10} T \exp[-1.10 \times 10^3/RT]$	(Estimate)	90
	>18		(Estimate)	102
	6		(Estimate)	96
		$F + Cl_2 \rightarrow FCl + Cl$		
		$6.2 \times 10^{12} T^{0.68} \exp[-0.5 \times 10^3/RT]$	(Estimate)	60, 105
	3	Log A = 13	(Estimate)	61
2000–2950		$>1 \times 10^{12}$	(Estimate)	104
225–375	1.4	Log A = 14.74	$N + NF_2$	16, 46
300		$(6.6 \pm 1.8) \times 10^{13}$	Microwave discharge CF_4	31
298		$(9.63 \pm 3.01) \times 10^{13}$	Microwave discharge F_2	103
		$F + Cl + M \rightarrow FCl + M$		
		$3 \times 10^{16} T^{-0.5}$ cm^6 mol^{-2} s^{-1}	(Estimate)	60
1779–2167		$(3.2$ to $6.4) \times 10^{13}$ cm^6 mol^{-2} s^{-1}	(Estimate)	108
	0	1.5×10^{15} cm^6 mol^{-2} s^{-1}	(Estimate)	106
		$F + HCl \rightarrow FH + Cl$		
1000–4000		$1.7 \times 10^{12} T^{0.5} \exp[-0.6 \times 10^3/RT]$	(Estimate)	89
	0.3		(Estimate)	96
		$1.9 \times 10^{12} T^{0.68} \exp[-0.6 \times 10^3/RT]$	(Estimate)	60, 105
298–2500		$9.3 \times 10^{11} T^{0.5} \exp[-0.6 \times 10^3/RT]$	(Estimate)	90
	1.2		(Estimate)	110
300		1.5×10^{13}	Flash photolysis WF_6, HF chemical laser	49
		7.3×10^{12}	$F_2 + NO$	44
257–353		$2.5 \times 10^{13} \exp[-0.9 \times 10^3/RT]$	Microwave discharge F_2	46
		$F + Br_2 \rightarrow FBr + Br$		
298		$\sim 5 \times 10^{13}$	$N + NF_2$	46
298		$(1.87 \pm 0.54) \times 10^{14}$	Microwave discharge F_2	103
		$F + HBr \rightarrow FH + Br$		
1000–4000		$1.0 \times 10^{12} T^{0.5} \exp[-0.4 \times 10^3/RT]$	(Estimate)	89
	0		(Estimate)	96
298–2500		$0.95 \times 10^{12} T^{0.5} \exp[-0.4 \times 10^3/RT]$	(Estimate)	90
273–360		$5 \times 10^{14} \exp[-1.5 \times 10^3/RT]$	Microwave discharge F_2	46
		$F + I_2 \rightarrow IF + I$		
298		$(2.59 \pm 0.66) \times 10^{14}$	Microwave discharge F_2	103
		$F + HI \rightarrow FH + I$		
298–4000		$1.1 \times 10^{12} T^{0.5} \exp[-0.4 \times 10^3/RT]$	(Estimate)	89, 90
	0		(Estimate)	96
		$F + ICl \rightarrow$ products		
298		$(3.01 \pm 1.2) \times 10^{14}$	Microwave discharge F_2	103
		$F + ClF \rightarrow F_2 + Cl$		
	0.4	$<10^{13}$	(Estimate)	106
		$F + ClF_2 \rightarrow F_2 + ClF$		
800–1300		1×10^{12}	(Estimate)	112
		$F + ClF_3 \rightarrow F_2 + ClF_2$		
800–1300		$0.75 \times 10^{11} \exp[-2.5 \times 10^3/RT]$	(Estimate)	112
		$F + ClF_4 \rightarrow F_2 + ClF_3$		
299–343	~0		(Estimate)	12, 113
		$F + ClF_4 \rightarrow ClF_5^*$		
299–343	~0		(Estimate)	12
		$F + ClF_5 \rightarrow F_2 + ClF_4$		
293	16.6		(Estimate)	113

and Schieler[90] arrived at an estimated rate constant of $k_{36} = 3.5 \times 10^{10} T \exp(-1100/RT)$ cm^3 mol^{-1} s^{-1}. Johnston and Parr[96] estimated 6 kcal mol^{-1} as the activation energy for the process, while O'Neil et al.,[102] using ab initio methods, predicted a much higher value of 18 kcal mol^{-1}. The results obtained for reaction 36 are included in Table VII.

B. Reaction with Chlorine and Hydrogen Chloride

The first report of the rate constant for the reaction

$$F + Cl_2 \rightarrow FCl + Cl \tag{37}$$

determined experimentally, was published by Warnatz et al.[16] They produced F atoms from the reaction of NF_2 with active nitrogen and from mass spectrometric analysis reported a value of $k_{37} = 5.5 \times 10^{14} \exp(-1400/RT)$ cm^3 mol^{-1} s^{-1}. In the same paper, they reported that since the concentration of Cl atoms produced corresponded to the concentration of F atoms present, reaction 37 proceeded directly, with virtually no FCl formed by the two-step process

$$F + Cl_2 \rightarrow FCl_2 \tag{38}$$

$$F + FCl_2 \rightarrow 2FCl \tag{39}$$

Clyne et al.[31] arrived at a value of 6.6×10^{13} cm^3 mol^{-1} s^{-1} for k_{37} at room temperature. Very recently,[103] this value has been revised to 9.63×10^{13} cm^3 mol^{-1} s^{-1}.

Estimates of k_{37} have been reported by Fletcher and Dahneke.[61] McIntyre and Diesen,[104] Bahn,[105] and Cherry et al.[60]

Wiersma and Fletcher[106] studied the reaction of F_2 with Cl_2 in an attempt to find the explosion limit of the mixture. Following dissociation of F_2, reactions 37 and 40–47 were considered as possible steps in the mechanism.

$$F + Cl_2 \rightarrow FCl + Cl \tag{37}$$

$$Cl + F_2 \rightarrow FCl + F \tag{40}$$

$$F + Cl + M \rightarrow FCl + M \tag{41}$$

$$F + F + M \rightarrow F_2 + M \tag{42}$$

$$Cl + Cl + M \rightarrow Cl_2 + M \tag{43}$$

$$Cl + FCl \rightarrow Cl_2 + F \tag{44}$$

$$F + FCl \rightarrow F_2 + Cl \tag{45}$$

$$Cl_2 + M \rightarrow 2Cl + M \tag{46}$$

$$FCl + M \rightarrow Cl + F + M \tag{47}$$

Steps 45, 46, and 47 were later eliminated as unimportant.

Bemand and Clyne[30] suggested that the relative rate constants of the reactions of F $^2P_{3/2}$ and F $^2P_{1/2}$ with chlorine could be measured by atomic resonance absorption spectrometry.

Schatz and Kaufman[107] reacted F atoms with Cl_2 and obtained a yellow luminescence which they attributed to the $A^3\Pi_{0^+} \rightarrow X^1\Sigma^+$ system of Cl_2. They suggested the following mechanism

$$F + Cl_2 \rightarrow FCl + Cl \tag{37}$$

$$Cl + Cl + M \rightarrow Cl_2\,(A^3\Pi_{0^+}) + M \tag{48}$$

$$Cl_2\,(A^3\Pi_{0^+}) \rightarrow Cl_2\,(X^1\Sigma^+) + h\nu \tag{49}$$

At the pressures used, step 48 was expected to be slow, and thus their observation of an extensive emission zone indicated that reaction 37 was very fast. In the same study, it was found that at 25 °C, reaction 40 was sufficiently slow that it did not affect the concentration of F_2. From this, it was suggested that reaction 36 could be used as a chemiluminescent titration for F atoms in the presence of F_2. Nordine[32] ruled out the termolecular recombination reaction 50

$$F + Cl + M \rightarrow FCl^* + M \tag{50}$$

which gives an excited FCl* molecule as a contributing factor in the chemiluminescence observed following the F + Cl_2 reaction. The reason given was that when the F atom concentration was increased relative to the Cl atom concentration, the intensity of the chemiluminescence did not increase.

TABLE VIII. Relative Rates of Halogen Reactions

Temp, °K	k_1/k_2[a]	Method	Ref
(1) F + HCl → FH + Cl; (2) F + CH_4 → FH + CH_3			
300	0.19 ± 0.02	Microwave discharge CF_4	33
	>8.67*	F_2 + NO	44
(1) F + HCl → FH + Cl; (2) F + HBr → FH + Br			
300	0.22*	Microwave discharge CF_4	33
(1) F + HCl → FH + Cl; (2) F + HI → FH + I			
300	0.16*	Microwave discharge CF_4	33
(1) F + HCl → FH + Cl; (2) F + NO → FNO*			
	1.28×10^3	F_2 + NO	44
(1) F + HCl → FH + Cl: (2) F + CH_3F → FH + CH_2F			
	7.36*	F_2 + NO	44
(1) F + HCl → FH + Cl; (2) F + CH_2F_2 → FH + CHF_2			
	1.97*	F_2 + NO	44
(1) F + HCl → FH + Cl; (2) F + CHF_3 → FH + CF_3			
	0.027*	F_2 + NO	44
(1) F + HCl → FH + Cl; (2) F + $CHClF_2$ → FH + CCl_2F			
	0.20*	F_2 + NO	44
(1) F + HCl → FH + Cl; (2) F + $CBrF_3$ → products			
	5.57×10^{-4} *	F_2 + NO	44
(1) F + HCl → FH + Cl; (2) F + NH_3 → products			
	7.72×10^{-2}*	F_2 + NO	44
(1) F + HCl → FH + Cl; (2) F + PH_3 → products			
	0.186*	F_2 + NO	44
(1) F + HBr → FH + Br; (2) F + HI → FH + I			
300	0.73*	Microwave discharge CF_4	33
(1) F + HBr → FH + Br; (2) F + CH_4 → FH + CH_3			
300	0.87 ± 0.14	Microwave discharge CF_4	33
(1) F + HI → FH + I; (2) F + HC≡CH → FHC═CH			
283	0.40	Neutron bombardment	45
283	0.37 ± 0.05	Neutron bombardment	78
(1) F + HI → FH + I; (2) F + C_2H_2 → FH + HC≡C			
283	3.33*	Neutron bombardment	45
283	2.64*	Neutron bombardment	78
(1) F + HI → FH + I: (2) F + C_2H_6 → FH + C_2H_5			
283	0.33*	Neutron bombardment	45
283	0.26*	Neutron bombardment	78
(1) F + HI → FH + I; (2) F + CH_4 → FH + CH_3			
283	0.93*	Neutron bombardment	45
283	0.90*	Neutron bombardment	78
300	1.2 ± 0.1	Microwave discharge CF_4	33
(1) F + HI → FH + I: (2) F + CD_4 → FD + CD_3			
283	1.48*	Neutron bombardment	45
283	1.54*	Neutron bombardment	78
(1) F + HI → FH + I; (2) F + CH_3CF_3 → FH + CH_2CF_3			
283	8.00*	Neutron bombardment	45
283	6.98*	Neutron bombardment	78
(1) F + HI → FH + I: (2) F + H_2S → FH + SH			
283	0.28*	Neutron bombardment	78
(1) F + ICl → FI + Cl: (2) F + ICl → FCl + I			
298	3.3 ± 0.7	Microwave discharge F_2	103

[a] Ratios marked with an asterisk, although not presented in the original reference, have been calculated from other ratios given in the reference.

Rate constants for the total termolecular recombination reaction

$$F + Cl + M \rightarrow FCl + M \tag{41}$$

which have been estimated by Wiersma and Fletcher.[106] Cherry et al.,[60] and Blauer et al.,[108] are included in Table VII. Fletcher and Dahneke[61] dismissed the activation energy of reaction 41 as being "very small" in their study of the overall reaction

$$F_2 + Cl_2 \rightarrow 2FCl \qquad (51)$$

This reaction was found to be first order in F_2 and one-half order in Cl_2.

The reaction of F atoms with HCl proceeds by H atom abstraction

$$F + HCl \rightarrow FH + Cl \qquad (52)$$

From measurements of the intensity of emission from an HF chemical laser, Kompa and Wanner[49] obtained a value of 1.5 × 10^{13} cm^3 mol^{-1} s^{-1} for the rate constant of reaction 52.

Pollock and Jones[44] arrived at a value of $k_{52} = 7.3 \times 10^{12}$ cm^3 mol^{-1} s^{-1} based on a comparison with the reaction

$$F + NO + M \rightarrow FNO^* + M \qquad (53)$$

This rate constant was determined from the ratio k_{52}/k_{53}, by observing the relative decrease in the intensity of the FNO^* emission by addition of HCl to the F + NO + M system. The absolute rate constant k_{52} was calculated from the value for k_{53} given by MacLean and co-workers.[109] Warnatz[46] studied the reaction of F atoms with HCl mass spectrometrically and arrived at a value of $k_{52} = 2.5 \times 10^{13} \exp(-900/RT)$ cm^3 mol^{-1} s^{-1}.

Estimations for k_{52} have been reported by Mayer et al.,[89,90] based on the hard-sphere collision theory, and by Bahn[105] and Cherry et al.[60] The activation energy for reaction 52 has also been estimated by Johnston and Parr[96] and by Jonathan et al.,[110] the latter using an Evans–Polanyi type relationship[111] between activation energy and exothermicity. The rate constants and activation energies for reaction 52 are included in Table VII. Relative rate constants for this reaction have also been determined[33,34] and are presented in Table VIII.

C. Reaction with Bromine and Hydrogen Bromide

Warnatz[46] reported an approximate value for the rate constant of the reaction of F atoms with Br_2 to be about 5 × 10^{13} cm^3 mol^{-1} s^{-1}. More recently, Appelman and Clyne[103] arrived at a rate constant of 1.87 × 10^{14} cm^3 mol^{-1} s^{-1}. The only other study to date on the F atom reaction with Br_2 was that by Schatz and Kaufman.[107] A yellow chemiluminescence was obtained when Br_2 was mixed with F atoms produced in an electrical discharge. The reaction mechanism was described as

$$F + Br_2 \rightarrow FBr\,(^3\Pi_{0^+}) + Br \qquad (54)$$

$$FBr\,(^3\Pi_{0^+}) \rightarrow FBr\,(X^1\Sigma) + h\nu \qquad (55)$$

Excited Br_2 produced by recombination of Br atoms would also be expected to give emission but at a wavelength beyond the sensitivity of their apparatus.

Jonathan et al.[33] found the rate constant for the reaction of F atoms with HBr relative to F + CH_4.

$$F + HBr \rightarrow FH + Br \qquad (56)$$

This value and several values of k_{56} relative to a number of other fluorine atom reactions, as calculated from results presented by Jonathan et al.,[33] are given in Table VIII.

Values for the absolute rate constant k_{56} have been estimated by Mayer et al.[89,90] and appear in Table VII. The only experimental study on reaction 56 was reported by Warnatz[46] who studied the reaction mass spectrometrically and arrived at a rate constant [$k_{56} = 5 \times 10^{14} \exp(-1500/RT)$ cm^3 mol^{-1} s^{-1}] which was much higher than the estimated values.

D. Reaction with Iodine and Hydrogen Iodide

The abstraction of I from I_2 by F atoms has been studied by Appelman and Clyne.[103] As in the analogous reactions with Br_2 and Cl_2, the rate is close to the hard-sphere bimolecular collision frequency. They report a value of 2.59 × 10^{14} cm^3 mol^{-1} s^{-1}.

No reports of experimentally measured absolute rate constants for the F + HI reaction have been published. Mayer et al.[89,90] have reported estimated values for the rate constant based on the hard-sphere collision theory.

Williams and Rowland[45,78] reported relative rate constants for the F + HI reaction compared to the addition reaction

$$F + HC{\equiv}CH \rightarrow FHC{=}CH \qquad (57)$$

using nearly thermal ^{18}F atoms. Jonathan et al.[33] found the rate constant for the F + HI reaction relative to the F + CH_4 reaction by a chemiluminescent method. These values, as well as relative rates for the F + HI reaction compared to other fluorine atom reactions calculated from these papers, appear in Table VIII.

E. Reaction with Interhalogen Compounds

The reaction of F atoms with ICl has been studied by Appelman and Clyne[103] who found a value of (3.01 ± 1.2) × 10^{14} cm^3 mol^{-1} s^{-1} for the overall reaction. The reaction proceeds along two different channels

$$F + ICl \rightarrow FI + Cl \qquad (58)$$

$$F + ICl \rightarrow FCl + I \qquad (59)$$

The ratio k_{58}/k_{59} is 3.3 ± 0.7.

All other reports on the reaction of F atoms with interhalogen compounds involve ClF_x molecules. Although no rate constants have been found experimentally, estimated rate constants or activation energies have been published for the reaction of F atoms with ClF,[106] ClF_2,[112] ClF_3,[112] and ClF_5.[113] All of the reactions involve a fluorine atom abstraction and the formation of F_2

$$F + ClF_x \rightarrow F_2 + ClF_{x-1} \qquad (60)$$

McIntyre and Diesen[104] studied the dissociation of ClF in shock tubes and considered the following reactions

$$F + ClF \rightarrow F_2 + Cl \qquad (45)$$

$$Cl + ClF \rightarrow Cl_2 + F \qquad (61)$$

Blauer et al.[108] considered reaction 61 to be unimportant.

The decomposition of ClF_3 was studied by Blauer et al.,[112] and the following steps were given consideration

$$ClF_3 + M \rightarrow ClF_2 + F + M \qquad (62)$$

$$ClF_2 + M \rightarrow ClF + F + M \qquad (63)$$

$$F + ClF_2 \rightarrow ClF + F_2 \qquad (64)$$

$$ClF_3 + ClF \rightarrow 2ClF_2 \qquad (65)$$

$$F + F + M \rightarrow F_2 + M \qquad (42)$$

$$F + ClF_3 \rightarrow ClF_2 + F_2 \qquad (66)$$

Schumacher and co-workers[12,114] reported the synthesis of ClF_5 from ClF_3 and F atoms. The F atoms were produced by photolysis of F_2 at 365 nm. The following mechanism was proposed:

$$F + ClF_3 + M \rightarrow ClF_4 + M \qquad (67)$$

$$F + ClF_4 \rightarrow ClF_5^* \qquad (68)$$

$$F + ClF_4 \rightarrow ClF_3 + F_2 \qquad (69)$$

$$ClF_5^* + ClF_3 \rightarrow 2ClF_4 \qquad (70)$$

$$ClF_5^* + M \rightarrow ClF_5 + M \qquad (71)$$

$$ClF_5^* \rightarrow ClF_4 + F \qquad (72)$$

$$F + F + M \rightarrow F_2 + M \qquad (42)$$

The authors predicted $k_{68} \approx k_{69}$ with the activation energy in each case approximately zero. Blauer et al.[115] showed that, in the thermal reaction of F atoms with ClF_3, the reverse of reactions 67 and 71 becomes important.

A summary of the absolute and relative rate constants for the reactions of F atoms with the interhalogens is presented in Tables VII and VIII, respectively.

VII. Reaction with Oxygen-Containing Compounds

A. Reaction with Oxygen and Ozone

The reaction of F atoms with O_2 has been the subject of very few reports. In studying the oxygen inhibition of the F + H_2 reaction, Levy and Copeland[93] estimated a value of $k \sim 10^{12.1}$ cm^6 mol^{-2} s^{-1} for the rate constant of the third-order reaction

$$F + O_2 + M \rightarrow FO_2 + M \qquad (73)$$

Milstein et al.[116] studied the rate of F atom addition to acetylene or ethylene relative to the rate of reaction of F atoms with O_2. ^{18}F atoms were produced by neutron bombardment of ^{19}F and reduced to thermal levels by collision with SF_6. The authors found that increasing the concentration of O_2 had little effect on the concentration of $CH_2CH_2\,^{18}F$ produced by the reaction

$$^{18}F + C_2H_4 \rightarrow CH_2CH_2{}^{18}F^* \qquad (74)$$

An upper limit to the ratio for the rate of reaction 75 to reaction 74 was reported to be $k_{75}/k_{74} \leq 0.006$.

$$^{18}F + O_2 \rightarrow {}^{18}FO_2 \qquad (75)$$

A value of $k_{75}/k_{76} \leq 0.005$ was also reported.

$$^{18}F + C_2H_2 \rightarrow CHCH^{18}F \qquad (76)$$

Arkell[117] and Spratley et al.[118] studied the reaction of F_2 with O_2 in matrices. They observed the vibrational spectra of the compounds FO_2 and F_2O_2 which, they suggested, were formed as in the following mechanism.

$$F + O_2 \rightarrow FO_2 \qquad (77)$$

$$F + FO_2 \rightarrow FOOF \qquad (78)$$

In addition, Arkell[117] reported the appearance of FO_4 following the reaction of F_2 and O_2 in an oxygen matrix. He suggested that one of the following reactions was responsible for the formation of FO_4.

$$F + O_2 \rightarrow FO_2 \xrightarrow{O_2} FO_4 \qquad (79)$$

$$F + O_4 \rightarrow FO_4 \qquad (80)$$

Chegodaev and Tupikov[119] showed that the decrease in the value of the rate constant for decomposition of FO_2 as the concentration of O_2 increased was due to the re-formation of FO_2 by the reaction

$$F + O_2 + M \rightarrow FO_2 + M \qquad (73)$$

Schumacher and co-workers were the first to study the thermal[120] and photochemical[10] reactions between molecular fluorine and ozone. The overall thermal reaction was found to be first order in O_3 and ¼th order in F_2. They hypothesized that F_2 reacted, not with O_3, but with decomposition intermediates such as O atoms or excited O_2.[120] The photochemical reaction[10] following initiation by photolysis of F_2 at 365 nm was stated to proceed by the route

$$F + O_3 \rightarrow FO + O_2 \qquad (81)$$

$$FO + O_3 \rightarrow F + 2O_2 \qquad (82)$$

$$F + O_3 \rightarrow FO_3 \rightarrow \tfrac{1}{2}F_2 + \tfrac{3}{2}O_2 \qquad (83)$$

An activation energy of about 3 kcal was estimated for reaction 81.

Kirshenbaum[121] reported that, at 120 K, the FO radicals formed in reaction 81, further reacted according to the scheme

$$FO + FO \rightarrow F_2O_2 \qquad (84)$$

$$F + FO \rightarrow F_2O \qquad (85)$$

$$FO + F_2 \rightarrow F_2O + F \qquad (86)$$

Reaction 81 has been extensively studied by Wagner and coworkers[27,122] and by Zetzsch.[47] The reaction was studied mass spectrometrically, with F atoms produced by microwave discharge through F_2 or CF_4 and by reaction of NF_2 with active nitrogen. The concentration of FO formed was found to be much lower when active nitrogen was used to produce the F atoms. This was attributed to the rapid reaction

$$N + FO \rightarrow NO + F \qquad (87)$$

The F atom concentration was also found to increase due to the bimolecular reaction

$$FO + FO \rightarrow 2F + O_2 \qquad (88)$$

Clyne and Watson[17] reported a rate constant of 10^{12}–10^{13} cm^3 mol^{-1} s^{-1} for reaction 88, following production of FO from F atoms and O_3. The ground-state FO radical was detected mass spectrometrically.

B. Reaction with Water and Hydroxyl Radical

Zetzsch[47] studied the reaction of F atoms with water, using mass spectrometry. A rate constant of $1.3 \times 10^{13} \exp(-400/RT)$ cm^3 mol^{-1} s^{-1} was reported for the reaction

$$F + H_2O \rightarrow FH + OH \qquad (89)$$

Fluorine atoms also react with the OH radical formed as in

$$F + OH \rightarrow FH + O \qquad (90)$$

At high initial F atom and H_2O concentrations, the subsequent reactions of OH radicals could also be monitored

$$OH + OH \rightarrow H_2O + O \qquad (91)$$

$$O + OH \rightarrow O_2 + H \qquad (92)$$

Schatz and Kaufman[107] observed the chemiluminescence obtained following the reaction of F atoms with water. The chemiluminescence was attributed to emission from the OH ($A^2\Sigma^+$) state which was formed by the three-body recombination of H and O atoms

$$F + H_2O \rightarrow FH + OH \qquad (89)$$

$$F + OH \rightarrow FH + O \qquad (90)$$

$$O + OH \rightarrow O_2 + H \qquad (92)$$

$$O + H + M \rightarrow OH\,(A^2\Sigma^+) + M \qquad (93)$$

$$OH\,(A^2\Sigma^+) \rightarrow OH\,(X^2\Pi) + h\nu \qquad (94)$$

C. Reaction with Oxygen–Halogen Compounds

The reaction of F_2 with ClO_2, studied by Aymonino et al.,[123] was reported to include an F atom reaction as a propagation step

$$F_2 + ClO_2 \rightarrow FClO_2 + F \qquad (95)$$

$$F + ClO_2 + M \rightarrow FClO_2 + M \qquad (96)$$

$$F + F + M \rightarrow F_2 + M \qquad (97)$$

$$F \xrightarrow{\text{wall}} \tfrac{1}{2}F_2 \qquad (98)$$

TABLE IX. Reaction with Oxygen-Containing Compounds

Temp, K	E, kcal mol^{-1}	k, cm^3 mol^{-1} s^{-1}	Method	Ref
		$F + O_2 + M \rightarrow FO_2 + M$		
		$\sim 10^{12.1}$ cm^6 mol^{-2} s^{-1}	(Estimate)	93
		$F + O_3 \rightarrow FO + O_2$		
298		$\sim 5 \times 10^{12}$	$N + NF_2$, microwave discharge CF_4, F_2	27
273–365	0.45	$\sim 1 \times 10^{13} \exp(-0.450 \times 10^3/RT)$	$N + NF_2$, microwave discharge CF_4, F_2	47
253–365	0.45	$1.7 \times 10^{13} \exp(-0.450 \times 10^3/RT)$	$N + NF_2$, microwave discharge CF_4, F_2	127
273–293	~3		$F_2 + O_3$	10
		$F + OH \rightarrow FH + O$		
1000–4000	0.20	$5 \times 10^{11} T^{1/2} \exp(-0.20 \times 10^3/RT)$	(Estimate)	89
298–2500	0.30	$4.6 \times 10^{11} T^{1/2} \exp(-0.30 \times 10^3/RT)$	(Estimate)	90
	0.2	$2.9 \times 10^{12} T^{0.68} \exp(-0.2 \times 10^3/RT)$	(Estimate)	60
	6.0	$5 \times 10^{11} T^{1/2} \exp(-6.0 \times 10^3/RT)$	(Estimate)	*a, b*
		$F + H_2O \rightarrow FH + OH$		
	0.6	$1.4 \times 10^{10} T^{0.68} \exp(-0.6 \times 10^3/RT)$	(Estimate)	60
	3		(Estimate)	96
243–365	0.4	$1.3 \times 10^{13} \exp(-0.4 \times 10^3/RT)$	$N + NF_2$	47
	7.0	$5 \times 10^{11} T^{1/2} \exp(-7.0 \times 10^3/RT)$	(Estimate)	*a, b*
	6.0	$10^{11} T^{1/2} \exp(-6.0 \times 10^3/RT)$	(Estimate)	*c*
	0.5	$5.6 \times 10^{11} T^{1/2} \exp(-0.5 \times 10^3/RT)$	(Estimate)	*d*
		$F + ClO_2 + M \rightarrow FClO_2 + M$		
227–299	4.1 ± 1.5		$F_2 + ClO_2$	123
		$F + F_2O \rightarrow FO + F_2$		
288–318	15		Photochemical reaction F_2O	124
293–545	14.3 ± 1.5		Photochemical reaction F_2O	125
501–583	13.7	$5.1 \times 10^{10} \exp[-(13.7 \pm 1.0) \times 10^3/RT]$	Thermal decomposition F_2O	126
		$F + FO_2 \rightarrow F_2 + O_2$		
	~3		(Estimate)	128
		$F + HOF \rightarrow HF + OF$		
298		$>1.2 \times 10^{14}$	Microwave discharge F_2	103
		$F + BrO_3F \rightarrow$ products		
298		$<4.2 \times 10^8$	Microwave discharge F_2	103
		(1) $F + O_2 \rightarrow FO_2$; (2) $F + C_2H_4 \rightarrow CH_2CH_2F$		
		$k_1/k_2 \leq 0.006$	Neutron bombardment	116
		(1) $F + O_2 \rightarrow FO_2$; (2) $F + C_2H_2 \rightarrow CHCHF$		
		$k_1/k_2 \leq 0.005$	Neutron bombardment	116

[a] S. W. Mayer, E. A. Cook, and L. Schieler, Aerospace Corp. Report TDR-269(4210-10)-6, 1964 as quoted in ref 5. [b] P. I. Gold, TRW Systems Report 5435-6005-TU000, 1965, as quoted in ref 5. [c] R. Tunder, S. W. Mayer, and L. Schieler, Aerospace Corp. Report TR-1001 (9210-02)-1, 1966, as quoted in ref 5. [d] S. W. Mayer and L. Schieler, Aerospace Corp. Report TR-669 (9210-02)-3, 1966, as quoted in ref 5.

A rate constant of $1.3 \times 10^{13} \exp(-8.0 \times 10^3/RT)$ cm^3 mol^{-1} s^{-1} was reported for k_{95}, and an activation energy of 4.1 ± 1.5 kcal for reaction 96.

Schumacher and co-workers[124–127] have studied both the thermal and photochemical decomposition of F_2O. In each case, a fluorine atom is produced either photochemically, reaction 99, or thermally, reaction 100, which reacts further with F_2O

$$F_2O + h\nu \rightarrow F + FO \quad (99)$$

$$F_2O + F_2O \xrightarrow{\Delta} F_2O + F + FO \quad (100)$$

$$F_2O + M \rightarrow F + FO + M \quad (101)$$

$$F + F_2O \rightarrow F_2 + FO \quad (102)$$

$$FO + FO \rightarrow O_2 + 2F \quad (88)$$

$$F + F + M \rightarrow F_2 + M \quad (97)$$

An activation energy of 14.3 ± 1.5 kcal for reaction 102 was determined from the photochemical investigation,[125] while the results of the thermal study[126] gave $k_{102} = 5.1 \times 10^{10} \exp[-(13.7 \pm 1.0) \times 10^3/RT]$ cm^3 mol^{-1} s^{-1}.

In a study of the reaction of fluorine with CF_2O, Lopez et al.[128] estimated the activation energy of the reactions

$$F + FO_2 \rightarrow F_2 + O_2 \quad (103)$$

to be about 3 kcal mol^{-1}.

Appelman and Clyne[103] reported on the rapid reaction between F atoms and HOF. The reaction proceeds by H atom abstraction followed by regeneration of F atoms

$$F + HOF \rightarrow HF + FO \quad (104)$$

$$2FO \rightarrow O_2 + 2F \quad (88)$$

Because of extraneous peak interference in the mass spectrograph, the authors were unable to obtain an absolute rate constant for reaction 104. However, they report a lower limit of 1.2 × 10^{14} cm^3 mol^{-1} s^{-1} for this rate constant.

In the same paper[103] they also reported that a reaction of F atoms with BrO_3F proceeded at too slow a rate to be measured. An upper limit of 4.2 × 10^8 cm^3 mol^{-1} s^{-1} was set for this rate constant.

A complete summary of the rate constants for the reactions of fluorine atoms with oxygen containing compounds is presented in Table IX.

VIII. Reaction with Nitrogen-Containing Compounds

A. Reaction with Nitrogen and Ammonia

With the exception of one report by Milstein et al.,[116] the reaction between molecular nitrogen and fluorine atoms has not been studied. During their investigation of the rate of reaction of thermal ^{18}F atoms with acetylene relative to the rate of ^{18}F atom reactions with a number of other compounds, they hypothesized that ^{18}F atoms and nitrogen could react to form $N_2{}^{18}F$. However, they were unable to prove this since, if the compound formed at all, it rapidly decomposed. An upper limit for k_{105}/k_{106} was set at 0.002.

$$^{18}F + N_2 \rightarrow N_2{}^{18}F \tag{105}$$

$$^{18}F + C_2H_2 \rightarrow C_2H_2{}^{18}F \tag{106}$$

The study of the reaction of F atoms with ammonia has been hampered by the production of a white solid, NH_4F, as an end product. This interference prevented Warnatz[46] from achieving more than an order of magnitude approximation for the rate constant of the hydrogen abstraction reaction

$$F + NH_3 \rightarrow FH + NH_2 \tag{107}$$

He reported k_{107} to be greater than 10^{13} cm^3 mol^{-1} s^{-1} with a corresponding activation energy of less than 2 kcal mol^{-1}.

The inhibition of the F_2/H_2 reaction by NH_3 as reported by Homann and MacLean[82] was also attributed to the formation of solid NH_4F. The flame profile of reaction products of the fluorine–ammonia system as studied mass spectrometrically by the same authors showed NF_2H, NH_2F, and NH_2 as reaction intermediates and NF_2, N_2, and HF as stable products. A mass peak for H_2F^+ was also observed, but the authors were unable to discern whether the parent species was H_2F or NH_4F.

Schatz and Kaufman[107] reported that the reaction of atomic fluorine with ammonia produced two chemiluminescent transitions. The NH ($A^3\Pi \rightarrow X^3\Sigma^-$) and the NF ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) transitions were observed. The production of excited NH was attributed to the recombination of thermal N and H atoms.

B. Reaction with Nitric Oxide, Nitrous Oxide, and Nitrogen Dioxide

The F_2–NO reaction has been studied in detail by a number of researchers. Johnston and Bertin[129] studied the absorption and emission spectra obtained following the reaction of F_2 with NO. The absorption spectrum occurred between 335 and 260 nm with a maximum at 311 nm, while a structureless emission was observed between 640 and 510 nm with a maximum at 609.5 nm. The emission was attributed to the chemiluminescent decay of FNO^*

$$NO + F_2 \rightarrow FNO + F \tag{108}$$

$$F + NO \rightarrow FNO^* \tag{109}$$

$$FNO^* + M \rightarrow FNO + M \tag{110}$$

$$FNO^* \rightarrow FNO + h\nu \tag{111}$$

Rapp and Johnston[130] found reaction 108 to be rate determining with $k_{108} \sim 6 \times 10^{10}$ cm^3 mol^{-1} s^{-1}, and estimated k_{109} to be 2 × 10^{14} cm^3 mol^{-1} s^{-1}. The rate constant for the reverse of reaction 108, k_{-108}, was believed to be about zero since the process is about 15 kcal endothermic.

The rate constants for the reaction of F atoms with NO in the presence of various third bodies

$$F + NO + M \rightarrow (1 - \alpha)FNO + \alpha FNO^* + M \tag{112}$$

were found by Kim et al.,[109,131] using ESR spectrometry to measure F atom concentrations, and by Skolnik et al.,[132] using the intensity of the emission from FNO^* as a measure of the F atom concentration. The rate constants, k_{112}, generally increase with the size of the third body M. Milstein et al.[116] found that the formation of FNO from F atom reaction with NO in the absence of a third body is virtually nonexistent. The rate constant, if the reaction occurred at all, was less than 1% of the value for the F atom addition reaction with acetylene (reaction 106).

Reaction 112 was used by Pollock and Jones[44] as a comparison reaction to find the rates of F atoms with a number of compounds. The rate constants for the reactions of F atoms with hydrocarbons and with group V hydrides were found to be greater than the rate constants for the reaction with NO by factors of 10^4 and 10^2–10^3, respectively.

Smardzewski and Fox[133] found that when F_2 and NO were photolyzed in a matrix, both FNO and NOF were formed. The latter was found to be a highly reactive species which rearranges to FNO upon further photolysis below 280 nm.

The reaction of F atoms with N_2O has been studied only in a matrix.[134,135] Rather than undergoing the more usual F atom addition, the process following photolysis of F_2 was found to be one of oxygen atom abstraction

$$F + N_2O \rightarrow FO + N_2 \tag{113}$$

$$F + FO \rightarrow F_2O \tag{114}$$

$$FO + F_2 \rightarrow F_2O + F \tag{115}$$

Attempts to produce a chemiluminescent species by reaction of F atoms with N_2O or NO_2 were unsuccessful,[107] probably because the substances reacted too slowly to produce enough light to be observed. Perrine and Johnston[136] found the reaction of F_2 with NO_2 to be first order in both compounds, with the rate constant $k = 1.59 \times 10^{12} \exp[-10.47 \times 10^3/RT]$ cm^3 mol^{-1} s^{-1}. Thus, the termolecular reaction

$$2NO_2 + F_2 \rightarrow 2NO_2F \tag{116}$$

was ruled out, and the following process proposed

$$F_2 + NO_2 \rightarrow F + NO_2F \tag{117}$$

$$F + NO_2 + M \rightarrow NO_2F + M \tag{118}$$

Reaction 118 was estimated to have a rate constant of about the same magnitude as that of the recombination reaction

$$F + F + M \rightarrow F_2 + M \tag{119}$$

C. Reactions with Nitrogen–Halogen Compounds

Warnatz[46] reacted F atoms with nitrosyl chloride and obtained a rate constant of 1.3 × 10^{12} cm^3 mol^{-1} s^{-1} at 298° for the reaction

$$F + NOCl \rightarrow FNO + Cl \tag{120}$$

The following steps were also included in the mechanism

$$Cl + NOCl \rightarrow NO + Cl_2 \tag{121}$$

$$F + Cl_2 \rightarrow FCl + Cl \tag{122}$$

Steps leading to the formation of NCl, OF, NF, or ClO are endothermic and were thereby eliminated.

Levy and Copeland,[137] using a colorimetric method, reported on the reaction of fluorine with the N_2F_4/NF_2 system. The fluorine

TABLE X. Reaction with Nitrogen-Containing Compounds

Temp, K	k, cm^3 mol^{-1} s^{-1}	E, kcal mol^{-1}	M	Method	Ref
	$F + NO + M \rightarrow FNO + M$ (k in cm^6 mol^{-2} s^{-1})				
193–297	2.8×10^{16}		Ar	Microwave discharge F_2	109
193–297	2.8×10^{16}		He	Microwave discharge F_2	109
193–297	1.1×10^{17}		NO	Microwave discharge F_2	109
195–288	$(2.99 \pm 0.18) \times 10^{16}$	~0	He	Microwave discharge F_2	131
195–288	$A = (4.5 \pm 4) \times 10^{16}$	0.2 ± 0.1	NO	Microwave discharge F_2	131
	$4.8 \pm 6.4 \times 10^{16}$		NO	Microwave discharge CF_4	132
	4.2×10^{16}		He	Microwave discharge CF_4	132
	$(2.5–3.2) \times 10^{16}$		Ar	Microwave discharge CF_4	132
	3.9×10^{16}		N_2	Microwave discharge CF_4	132
	1.3×10^{17}		CO_2	Microwave discharge CF_4	132
	1.6×10^{17}		CF_4	Microwave discharge CF_4	132
	1.4×10^{17}		SF_6	Microwave discharge CF_4	132
	1.1×10^{17}		C_2F_6	Microwave discharge CF_4	132
	$F + NO \rightarrow FNO$				
	2×10^{14}			(Estimate)	130
	$F + FNO \rightarrow$ products				
	0			(Estimate)	130
	$F + NH \rightarrow FH + N$				
298–2500	$5.2 \times 10^{11} T^{0.5} \exp[-1.0 \times 10^3/RT]$			(Estimate)	90
1000–4000	$5 \times 10^{11} T^{0.5} \exp[-0.4 \times 10^3/RT]$			(Estimate)	89
	$1.4 \times 10^{12} T^{0.68} \exp[-0.6 \times 10^3/RT]$			(Estimate)	*a*
	$F + NH_2 \rightarrow FH + NH$				
	$1.0 \times 10^{10} T^{0.68} \exp[-1.0 \times 10^3/RT]$			(Estimate)	*b, c*
	$6.2 \times 10^{11} T^{1/2} \exp[-0.9 \times 10^3/RT]$			(Estimate)	*d*
	$F + NH_3 \rightarrow FH + NH_2$				
298	$>10^{13}$	<2.0		Microwave discharge F_2	46
	$4.3 \times 10^{11} T^{0.5} \exp[-0.8/RT]$			(Estimate)	*d*
	$F + HNO \rightarrow FH + NO$				
	$2.4 \times 10^{11} T^{1/2}$			(Estimate)	*d*
	$F + NOCl \rightarrow FNO + Cl$				
298	1.3×10^{12}			Microwave discharge F_2	46
	$F + NF_3 \rightarrow F_2 + NF_2$				
	$8.8 \times 10^{13} \exp[-35.6 \times 10^3/RT]$			(Estimate)	139
	$F + NF_2 + M \rightarrow NF_3 + M$				
298	3.23×10^{17} cm^6 mol^{-2} s^{-1}			$NF_2 + N$	18

[a] R. Tunder, S. W. Mayer, and L. Schieler, Aerospace Corp. Report TR-1001(9210-02)-1 as quoted in ref 5. [b] S. W. Mayer and L. Schieler, Aerospace Corp. Report TDR-669(9210-02)-2, 1966, as quoted in ref 5. [c] L. Schieler and S. W. Mayer, Chemical Propulsion Information Agency Publication No. 108, 1966, p. 131, as quoted in ref 5. [d] S. W. Mayer and L. Schieler, Aerospace Corp. Report TDR-669(9210-02)-3, 1966, as quoted in ref 5.

atoms produced reacted with either NF_2 or N_2F_4 according to the mechanism

$$N_2F_4 + M \rightleftarrows 2NF_2 + M \quad (123)$$

$$NF_2 + F_2 \rightarrow NF_3 + F \quad (124)$$

$$F + NF_2 + M \rightarrow NF_3 + M \quad (125)$$

$$F + N_2F_4 \rightarrow NF_3 + NF_2 \quad (126)$$

Whether reaction 125 or 126 or both were occurring could not be determined from their experiments. Diesen[138] included the reverse of reaction 124

$$F + NF_3 \rightarrow NF_2 + F_2 \quad (127)$$

as an important step at high temperatures (1400–2000 K). MacFadden and Tschuikow-Roux[139] estimated k_{127} to be $8.8 \times 10^{13} \exp[-35.6 \times 10^3/RT]$ cm^3 mol^{-1} s^{-1}. Clyne and Watson,[18] while studying the reaction of F atoms with NF_2 by means of mass spectrometric sampling of free radicals from a discharge-flow system, stated that at room temperature reaction

TABLE XI. Relative Rates of Nitrogen-Containing Reactions

k_1/k_2	Method	Ref.
(1) $^{18}F + N_2 \rightarrow {}^{18}FN_2$; (2) $^{18}F + C_2H_2 \rightarrow CHCH^{18}F$ ≤ 0.002	Neutron bombardment	116
(1) $^{18}F + NO \rightarrow {}^{18}FNO$; (2) $^{18}F + C_2H_2 \rightarrow CHCH^{18}F$ ≤ 0.01	Neutron bombardment	116
(1) $F + NO \rightarrow FNO^*$; (2) $F + CH_4 \rightarrow FH + CH_3$ $\leq 0.9 \times 10^{-4}$	$F_2 + NO + CH_4$	44
(1) $F + NO \rightarrow FNO^*$; (2) $F + CH_3F \rightarrow FH + CH_2F$ $(1.06 \pm 0.18) \times 10^{-4}$	$F_2 + NO + CH_3F$	44
(1) $F + NO \rightarrow FNO^*$: (2) $F + CH_2F_2 \rightarrow FH + CHF_2$ $(3.96 \pm 0.52) \times 10^{-4}$	$F_2 + NO + CH_2F_2$	44
(1) $F + NO \rightarrow FNO^*$; (2) $F + CHF_3 \rightarrow FH + CF_3$ $(291 \pm 8) \times 10^{-4}$	$F_2 + NO + CHF_3$	44
(1) $F + NO \rightarrow FNO^*$; (2) $F + CHClF_2 \rightarrow FH + CClF_2$ $(38.9 \pm 0.8) \times 10^{-4}$	$F_2 + NO + CHClF_2$	44
(1) $F + NO \rightarrow FNO^*$; (2) $F + HCl \rightarrow FH + Cl$ $(7.8 \pm 0.7) \times 10^{-4}$	$F_2 + NO + HCl$	44
(1) $F + NO \rightarrow FNO^*$; (2) $F + CBrF_3 \rightarrow$ products 1.4 ± 0.5	$F_2 + NO + CBrF_3$	44
(1) $F + NO \rightarrow FNO^*$; (2) $F + NH_3 \rightarrow FH + NH_2$ $(1.01 \pm 0.004) \times 10^{-2}$	$F_2 + NO + NH_3$	44
(1) $F + NO \rightarrow FNO^*$; (2) $F + PH_3 \rightarrow$ products $(4.2 \pm 0.4) \times 10^{-3}$	$F_2 + NO + PH_3$	44

127 was unimportant. They obtained a rate constant of 3.23 × 10^{17} cm^6 mol^{-2} s^{-1} for reaction 125.

A complete summary of the absolute and relative rate constants of reactions of F atoms with nitrogen-containing compounds is given in Tables X and XI, respectively.

IX. Reaction with Carbon-, Carbon–Oxygen-, and Carbon–Nitrogen-Containing Compounds

A. Reaction with Carbon

Rosner and Strakey[140] reported that in the reaction of F atoms with pyrolytic graphite, the carbon atom removal probability is $\frac{1}{4}$, indicating that each F atom is used in the production of CF_4.

B. Reaction with CO-Containing Compounds

Schatz and Kaufman[107] reported that both CO and CO_2 react too slowly with F atoms to produce chemiluminescence. Milstein et al.[116] found the addition of ^{18}F atoms to CO to be at least 100 times slower than the addition of ^{18}F atoms to acetylene. The reaction with CO would be expected to produce ^{18}FCO, since abstraction of either a carbon or oxygen atom would be too endothermic to occur.

Milligan et al.[141] found that the photochemical reaction

$$F + CO \rightarrow FCO \tag{128}$$

occurred in matrices even when the CO concentration was small, indicating a low activation energy. Infrared studies also indicated the presence of F_2CO and $(FCO)_2$, and the following mechanism was proposed:

$$F + FCO \rightarrow F_2CO \tag{129}$$

$$FCO + FCO \rightarrow (FCO)_2 \tag{130}$$

Wang and Jones[42] flash-photolyzed mixtures of N_2F_4, CO, and N_2, producing the FCO radical by reaction 128. The absorption spectrum was observed between 220 and 340 nm. Decay of the FCO spectrum after 50 μs was followed by the observation of spectra attributed to F_2CO and $(FCO)_2$ presumably formed by reactions 129 and 130.

Schumacher and co-workers[142] showed that molecular fluorine and CO react to form FCO and an F atom, followed by reaction 128.

Appelman and Clyne[103] found the rate constant of the three-body recombination reaction of F atoms with CO to be 1.23 × 10^{16} cm^6 mol^{-2} s^{-1} with helium as third body, and 2.07 × 10^{16} cm^6 mol^{-2} s^{-1} with argon as a third body. The mechanism was suggested to be

$$F + CO + M \rightarrow FCO + M \tag{131}$$

$$2FCO \rightarrow CO + F_2CO \tag{132}$$

Arkell[135] reported that photolysis of F_2 and CO_2 in a nitrogen matrix at 4 K produced no reaction. However, Schumacher and co-workers[143] found the gas-phase photolysis possible, although the F + CO_2 reaction was not favored. They proposed the following mechanism

$$F_2 + h\nu \rightarrow 2F \tag{133}$$

$$F + CO_2 + M \rightarrow FCO_2 + M \tag{134}$$

$$FCO_2 \xrightarrow[F_2]{F} CF_3OF + \tfrac{1}{2}O_2 \tag{135}$$

$$F + F + M \rightarrow F_2 + M \tag{136}$$

$$F \xrightarrow{\text{wall}} SiF_4 + \tfrac{1}{2}O_2 \tag{137}$$

$$F + O_2 \rightarrow FO_2 \tag{138}$$

$$F + FO_2 \rightarrow F_2 + O_2 \tag{139}$$

The rate constant ratio k_{134}/k_{136} was estimated at 10^{-6}, and the activation energy of step 134 was 10.9 ± 0.3 kcal mol^{-1}, indicating that F atoms were more likely to recombine than to react with CO_2.

The photochemical reaction of F_2 with CF_2O was studied by Lopez et al.[128] After the initiation by reaction 133, the following reactions were proposed:

$$F + CF_2O \rightarrow CF_2OF \tag{140}$$

$$CF_2OF + CF_2OF \rightarrow (CF_2OF)_2^* \tag{141}$$

$$(CF_2OF)_2^* \xrightarrow[\text{conversion}]{\text{internal}} (CF_2OF)_2' \tag{142}$$

$$(CF_2OF)_2^* \xrightarrow{\text{wall}} CF_3OF + CF_2O \tag{143}$$

$$(CF_2OF)_2^* + CF_2O \rightarrow (CF_3O)_2 + CF_2O \tag{144}$$

$$(CF_2OF)_2' + F_2 \rightarrow 2CF_3OF \tag{145}$$

$$F \xrightarrow{\text{wall}} \tfrac{1}{2}F_2 \tag{146}$$

$$F + O_2 \rightarrow FO_2 \tag{138}$$

$$F + FO_2 \rightarrow F_2 + O_2 \tag{139}$$

The activation energy for step 140 was reported as 6.2 kcal mol^{-1}.

C. Reaction with CN-Containing Compounds

Milligan and Jacox[144] studied the matrix reaction of F_2 and F atoms with NCN. Infrared spectroscopy showed that the following reactions took place:

$$F_2 + NCN \rightarrow NF_2CN \tag{147}$$

$$F + NCN \rightarrow FNCN \tag{148}$$

Warnatz[46] reported on the gas-phase reactions of F atoms with cyanogen and with HCN. Mass spectrometry was used to determine the products and concentrations. The reaction with

TABLE XII. Rate Constants for Carbon-Containing Compounds

Temp. K	k, cm^3 mol^{-1} s^{-1}	Method	Ref
	$F + CO + He \rightarrow FCO + He$		
298	$(1.23 \pm 0.36) \times 10^{16}$ cm^6 mol^{-2} s^{-1}	Microwave discharge F_2 $[He]_{av} = 8.4 \times 10^{-8}$ mol cm^{-3}	103
	$F + CO + Ar \rightarrow FCO + Ar$		
298	$(2.07 \pm 0.72) \times 10^{16}$ cm^6 mol^{-2} s^{-1}	Microwave discharge F_2 $[Ar]_{av} = 9.4 \times 10^{-8}$ mol cm^{-3}	103
	$F + CO_2 + M \rightarrow FCO_2 + M$		
353–408	$E = 10.9 \pm 0.3$ kcal mol^{-1}	Photochemical reaction	143
	$F + CF_2O \rightarrow CF_2OF$		
288–353	$E = 6.2$ kcal mol^{-1}	Photochemical reaction	128
	$F + (CN)_2 \rightarrow FCN + CN$		
298	$<10^4$	(Estimate)	46
	$F + (CN)_2 \rightarrow F(CN)_2$		
298	2×10^{11}	$N + NF_2$, microwave discharge CF_4	46
	$F + HCN \rightarrow HCNF$		
298	7×10^{10}	$N + NF_2$, microwave discharge CF_4, F_2	46

cyanogen is not analogous to the Cl_2 and Br_2 reactions where abstraction of a halogen atom occurs, since for cyanogen, the abstraction reaction

$$F + (CN)_2 \rightarrow FCN + CN \tag{149}$$

would be endothermic and would be expected to have a rate constant $<10^4$ cm^3 mol^{-1} s^{-1}. However, the rate constant found for the removal of cyanogen by F atoms was $k = 2 \times 10^{11}$ cm^3 mol^{-1} s^{-1}, indicating the actual reaction to be

$$F + (CN)_2 \rightarrow F(CN)_2 \tag{150}$$

$$F + F(CN)_2 \rightarrow 2FCN \tag{151}$$

The reaction of F atoms with HCN[46] has a measured rate constant of 7×10^{10} cm^3 mol^{-1} s^{-1}. Hydrogen atom abstraction was eliminated since it would be followed by $(CN)_2$ formation which did not occur.

$$F + HCN \rightarrow HF + CN \tag{152}$$

$$CN + CN \rightarrow (CN)_2 \tag{153}$$

The replacement of H by F was also ruled out as being too endothermic (8 kcal mol^{-1}). The correct mechanism was postulated to be

$$F + HCN \rightarrow HCNF \tag{154}$$

$$F + HCNF \rightarrow HF + FCN \tag{155}$$

Vanpee et al.[145] found from the spectrum produced by a $(CN)_2/F_2$ flame that virtually all the fluorine present in the flame was atomic. The CN spectrum was observed to persist in the plume of the flame. Despite the observation of a number of CF radicals and relatively large amounts of FCN, they concluded that the reaction of F atoms with CN was not favorable.

A complete summary of the rate constants derived for reactions of fluorine atoms with CO and CN containing compounds appears in Table XII.

X. Reaction with Sulfur-Containing Compounds

The majority of the work on F atom reactions with compounds containing sulfur has come from the laboratory of Schumacher. The photochemical reaction with SO_3 was found to undergo the following reactions after photolytic production of F atoms from F_2.[146]

$$F + SO_3 \rightarrow FSO_3 \tag{156}$$

$$2FSO_3 \rightarrow F_2S_2O_6 \tag{157}$$

k_{156} was found to be much larger than the fluorine atom homogeneous recombination reaction.[147] Later, an additional reaction was shown to be important.[148]

$$F + FSO_3 \rightarrow F_2SO_3 \tag{158}$$

The ratio k_{157}/k_{158} was reported to be $(3.0 \pm 0.2) \times 10^{-2}$, while the activation energies for reactions 157 and 158 were said to be about zero.

The photochemical reaction of fluorine with F_2SO, following photolysis of F_2, was found to involve the following reactions[149]

$$F + F_2SO \rightarrow F_3SO \tag{159}$$

$$F_3SO + F_2 \rightarrow F_4SO + F \tag{160}$$

$$2F_3SO \rightarrow F_4SO + F_2SO \tag{161}$$

while the thermal reaction[150] also includes the step

$$F_2 + F_2SO \rightarrow F_3SO + F \tag{162}$$

Clyne and Watson[18] detected the SF ground-state radical mass spectrometrically in the reaction of F atoms with OCS in a flow system.

$$F + OCS \rightarrow SF + CO \tag{163}$$

The observed decrease in the SF concentration downstream was accounted for by the reaction

$$SF + SF \rightarrow SF_2 + S \tag{164}$$

The reaction of thermal ^{18}F atoms with SO_2 was studied by Milstein et al.,[116] who proposed (165a) and (165b) as possible reactions.

$$^{18}F + SO_2 \rightarrow {}^{18}FSO_2 \tag{165a}$$

$$^{18}F + SO_2 \rightarrow {}^{18}FO + SO \tag{165b}$$

They compared the sum of the rate constants $k_{165a} + k_{165b}$ with that of the addition reaction with acetylene

$$^{18}F + C_2H_2 \rightarrow FH_2C{=}CH_2 \tag{166}$$

and found $k_{165}/k_{166} = 0.04 \pm 0.02$.

Williams and Rowland[78] gave the ratio $k_{167}/k_{166} = 1.30 \pm 0.10$.

$$^{18}F + H_2S \rightarrow H^{18}F + SH \tag{167}$$

Schatz and Kaufman[107] observed no chemiluminescence from the reactions of fluorine atoms with H_2S or SO_2.

XI. Reaction with Organic Compounds

Studies made on the reaction of F_2 with organic compounds

TABLE XIII. Chemiluminescent Spectra Obtained from the Reaction of F Atoms with Hydrocarbons[a]

Species	Transition	Intensity
CF[b]	$(A^2\Sigma^+ \rightarrow X^2\Pi, v' = 0, 1)$	Medium
CF[b]	$(B^2\Delta \rightarrow X^2\Pi, v' = 0)$	Medium
CF_2[b]		Medium
CO[b,c] (fourth positive)	$(A^1\Pi \rightarrow X^1\Sigma^+, v' = 2–10)$	Medium
CO[c,d] (Cameron system)	$(a^3\Pi \rightarrow X^1\Sigma^+, v' = 0–5)$	Medium
C_2 (Swan bands)	$(d^1\Sigma_u^+ \rightarrow a^1\Sigma_q^+, v' = 0\leftarrow 5)$	Strong
CH	$(A^2\Delta \rightarrow X^2\Pi, v' = 0)$	Strong
C_3[d]		Weak
OH[c]	$(A^2\Sigma^+ \rightarrow X^2\Pi, v' = 0–3)$	Variable
CN[c]	$(B^2\Sigma^+ \rightarrow X^2\Sigma^+, v' = 0–4)$	Variable

[a] Compiled from ref 107. [b] Only from F_2–Ar. F atom source. [c] From impurity. [d] Only from CF_4–Ar. F atom source.

up to 1948 have been reviewed by Bigelow.[151] These reactions all involved molecular fluorine, but atomic fluorine reactions were intermediate steps in many cases. Some atomic fluorine-organic reactions have been included in reviews by Fettis and Knox,[1] and by Wagner and Wolfrum,[2] but these are incomplete.

Schatz and Kaufman[107] reported on the chemiluminescent spectra obtained when F atoms reacted with the hydrocarbons CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, 1,3-butadiene, and benzene. A summary of emission observed appears in Table XIII. In some cases, the presence or absence of emission depended upon whether the F atom source was a discharge through CF_4 or F_2.

A. Reaction with Saturated Hydrocarbons

The reaction of an F atom with a saturated hydrocarbon results in the abstraction of an H atom. A number of comparisons[8,9,13,72] have been made of the relative rates of abstraction from various saturated hydrocarbons. The relative rate constants appear in Table XIV. Absolute rate constants were found from these relative rates by comparison with values for the abstraction of H by F atoms from methane[19] or ethane.[9,152] In general, the rate constants for abstraction follow the order, primary hydrogen > secondary hydrogen > tertiary hydrogen. Activation energies are nearly zero for reactions involving alkanes with three or more carbon atoms.

Recently, there have been a number of studies on the kinetics of the reaction of F atoms with methane. Wagner et al.[19] and Zetzsch[47] studied the reaction in a fast-flow system by mass spectrometry. A rate constant of $3.3 \times 10^{14} \exp(-1150/RT)$ cm^3 mol^{-1} s^{-1} was determined. Since F atoms were produced from the reaction of NF_2 with active nitrogen, the mechanism of the reaction depended upon the concentration of active nitrogen. With a high concentration of N, the proposed mechanism was

$$F + CH_4 \rightarrow HF + CH_3 \tag{168}$$

$$N + CH_3 \rightarrow HCN + 2H \tag{169}$$

With a low concentration of active nitrogen, reaction 168 was followed by

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \tag{170}$$

The fact that CH_3 did not seem to react with F atoms indicated an upper limit of $k < 3 \times 10^{13}$ cm^3 mol^{-1} s^{-1} for the reaction

$$F + CH_3 \rightarrow \text{products} \tag{171}$$

The earlier work of Mercer and Pritchard,[7] on the reaction of molecular fluorine with methane indicated that reaction 168 was followed by

$$F_2 + CH_3 \rightarrow CH_3F + F \tag{172}$$

Foon and Reid[72] obtained a value of 1.8 kcal mol^{-1} for the activation energy of reaction 168, which was about 0.6 kcal mol^{-1} greater than values reported earlier. They explained this discrepancy by saying that their result was free of self-heating errors.

Kompa and Wanner[49] obtained a value of 4.3×10^{13} cm^3 mol^{-1} s^{-1} for k_{168} using the intensity of the HF chemical laser produced by the reaction of fluorine atoms with methane. Pollock and Jones[44] found $k_{168} \geq 6 \times 10^{13}$ cm^3 mol^{-1} s^{-1} based on the relative rate of the reaction of F atoms with NO. Wolfrum[153] set a lower limit of 5×10^{12} cm^3 mol^{-1} s^{-1} for k_{168}. Clyne et al.[31] found a value of 3.6×10^{13} cm^3 mol^{-1} s^{-1} for k_{168} using a mass spectrometer and the F + ClNO titration reaction as a measure of F atom concentration.

In addition to the relative rate constants presented in Table XIV, where various saturated hydrocarbons are compared, the rate of hydrogen abstraction from methane has been compared to a number of other substances by several authors. Jonathan et al.[33] found k_{168} to be greater than the rate constant for abstraction of H atoms from HCl, HBr, and H_2, but smaller than that for HI. These results appear in Tables IV and VIII. Williams and Rowland,[45,78] using nearly thermal ^{18}F atoms, measured the rate constants of reactions of F atoms with CH_4, CD_4 and C_2H_6 relative to the rate constant of the addition reaction

$$F + HC{\equiv}CH \rightarrow FHC{=}CH \tag{173}$$

The rate of reaction 168 relative to the rate of the reaction

$$F + CD_4 \rightarrow FD + CD_3 \tag{174}$$

has been studied by Foon et al.[74] using a competitive method with gas chromatographic analysis. They suggested that quantum mechanical tunneling does not play a role in these reactions.

The rate of H abstraction vs. D abstraction by F atoms from CH_2D_2 has been studied by Persky[154] using a fast flow system and mass spectrometric analysis. The ratio $k_{\text{H abstraction}}/k_{\text{D abstraction}}$ was found to be $(0.81 \pm 0.03) \exp[(275 \pm 15)/RT]$.

These results as well as values for the various relative rates for the reaction of F atoms with CH_4, CD_4, and C_2H_6 as calculated from the results of Williams and Rowland[45,78] appear in Table XIV.

A mass spectrometric analysis of the reaction of F atoms with ethane by Zetzsch[47] revealed the products HF, C_2H_4, C_4H_{10}, CH_3F, C_2H_5F, and C_3H_7F. The following mechanism was proposed

$$F + C_2H_6 \rightarrow C_2H_5 + HF \tag{175}$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \tag{176}$$

$$F + C_2H_5 \rightarrow CH_3 + CH_2F \tag{177}$$

$$CH_2F + CH_2F \rightarrow C_2H_4F_2 \tag{178}$$

$$CH_2F + CH_2F \rightarrow C_2H_3F + HF \tag{179}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{180}$$

$$CH_3 + CH_2F \rightarrow C_2H_5F \tag{181}$$

$$CH_3 + CH_2F \rightarrow C_2H_4 + HF \tag{182}$$

Cochran et al.[155] used ESR to study the reaction of F atoms with CH_4, C_2H_6, C_3H_8, and CH_3OH in argon matrices at 4 K. The methane and ethane abstractions produced HF and CH_3 or C_2H_5 as expected. The F atom propane reaction abstracted a primary hydrogen leaving an excited radical which decomposed:

$$F + C_3H_8 \rightarrow HF + p\text{-}C_3H_7^* \tag{183}$$

$$p\text{-}C_3H_7^* \rightarrow CH_3 + C_2H_4 \tag{184}$$

Methanol also underwent hydrogen abstraction

$$F + CH_3OH \rightarrow CH_2OH + HF \tag{185}$$

TABLE XIV. Relative Rates with Saturated Hydrocarbons

Temp, K	k_1/k_2	Method	Ref
	(1) F + C_2H_6 → FH + C_2H_5; (2) F + CH_4 → FH + CH_3		
198–351	$(0.38 \pm 0.04) \exp[(928 \pm 41)/RT]$	F_2 + hydrocarbons	9
283	3.41[a]	Neutron bombardment	78
283	2.79[a]	Neutron bombardment	45
273–358	$0.24 \exp[(1370 \pm 220)/RT]$	Competitive method F_2 + hydrocarbons	72
	(1) F + C_2H_6 → FH + C_2H_5; (2) F + C_3H_8 → FH + $CH_3CH_2CH_2$		
213–293	$(1.84 \pm 0.05) \exp[-(279 \pm 12)/RT]$	F_2 + hydrocarbons	9
273–348	$(1.68 \pm 0.04) \exp[-(470 \pm 20)/RT]$	Competitive method F_2 + hydrocarbons	72
	(1) F + C_3H_8 → FH + $CH_3CH_2CH_2$; (2) F + *n*-C_4H_{10} → FH + $CH_3(CH_2)_2CH_2$		
213–293	1.11 ± 0.06	F_2 + hydrocarbons	9
293–348	1.10 ± 0.09	Competitive method F_2 + hydrocarbons	72
	(1) F + C_3H_8 → FH + $(CH_3)_2CH$; (2) F + *n*-C_4H_{10} → FH + $CH_3CHCH_2CH_3$		
213–293	0.56 ± 0.04	F_2 + hydrocarbons	9
	(1) F + *i*-C_4H_{10} → FH + $CH_3CH(CH_3)CH_2$; (2) F + *n*-C_4H_{10} → FH + $CH_3(CH_2)_2CH_2$		
213–293	1.57 ± 0.06	F_2 + hydrocarbons	9
	(1) F + *n*-C_4H_{10} → FH + $CH_3(CH_2)_2CH_2$; (2) F + c-C_3H_6 → FH + c-C_3H_5		
213–293	1.02 ± 0.06	F_2 + hydrocarbons	9
	(1) F + *n*-C_4H_{10} → FH + $CH_3CHCH_2CH_3$; (2) F + c-C_3H_6 → FH + c-C_3H_5		
213–293	0.80 ± 0.06	F_2 + hydrocarbons	9
	(1) F + *neo*-C_5H_{12} → FH + $CH_3(CH_2)_3CH_2$; (2) F + *n*-C_4H_{10} → FH + $CH_3(CH_2)_2CH_2$		
293	1.8 ± 0.2	F_2 + hydrocarbons	13
	(1) F + C_3H_8 → FH + $CH_3CH_2CH_2$; (2) F + c-C_3H_6 → FH + c-C_3H_5		
213–293	1.13 ± 0.15	F_2 + hydrocarbons	9
	(1) F + C_3H_8 → FH + $(CH_3)_2CH$; (2) F + c-C_3H_6 → FH + c-C_3H_5		
213–293	0.45 ± 0.05	F_2 + hydrocarbons	9
	(1) F + *neo*-C_5H_{12} → FH + $CH_3(CH_2)_3CH_2$; (2) F + *i*-C_4H_{10} → FH + $CH_3(CH_2)_2CH_2$		
213–293	1.22 ± 0.04	F_2 + hydrocarbons	9
	(1) F + C_3H_8 → FH + $CH_3CH_2CH_2$: (2) F + C_3H_8 → FH + $(CH_3)_2CH$		
174–309	2.48 ± 0.08	F_2 + hydrocarbons	9
293–348	2.30 ± 0.41	Competitive method F_2 + hydrocarbons	72
	(1) F + *n*-C_4H_{10} → FH + $CH_3(CH_2)_2CH_2$; (2) F + *n*-C_4H_{10} → FH + $CH_3CHCH_2CH_3$		
213–298	1.30 ± 0.09	F_2 + hydrocarbons	9
293–348	2.43 ± 0.28	Competitive method F_2 + hydrocarbons	72
298–459	$0.91 \exp[-(97 \pm 20)/RT]$	F_2 + hydrocarbons	8
209–291	1.32 ± 0.03	F_2 + hydrocarbons	13
	(1) F + *i*-C_4H_{10} → FH + $CH_3CH(CH_3)CH_2$; (2) F + *i*-C_4H_{10} → FH + $(CH_3)_3C$		
213–293	6.41 ± 0.34	F_2 + hydrocarbons	9
298	0.72 ± 0.09	F_2 + hydrocarbons	8
	(1) ^{18}F + CH_4 → ^{18}FH + CH_3; (2) ^{18}F + C_2H_2 → $CH^{18}F{=}CH$		
283	0.41 ± 0.04	Neutron bombardment	78
283	0.43 ± 0.04	Neutron bombardment	45
	(1) ^{18}F + CD_4 → ^{18}FD + CD_3; (2) ^{18}F + C_2H_2 → $CH^{18}F{=}CH$		
283	0.24 ± 0.04	Neutron bombardment	78
283	0.27 ± 0.04	Neutron bombardment	45
	(1) ^{18}F + C_2H_6 → ^{18}FH + C_2H_5; (2) ^{18}F + C_2H_2 → $CH^{18}F{=}CH$		
283	1.40 ± 0.12	Neutron bombardment	78
283	1.20 ± 0.2	Neutron bombardment	45
	(1) F + CH_4 → FH + CH_3; (2) F + CD_4 → FD + CD_3		
283	1.71[a]	Neutron bombardment	78
283	1.59[a]	Neutron bombardment	45
	$(1.0 \pm 0.3) \exp[(230 \pm 200)/RT]$	F_2 + hydrocarbons	74
	(1) F + C_2H_6 → FH + C_2H_5: (2) F + CD_4 → FD + CD_3		
283	5.88[a]	Neutron bombardment	78
283	4.34[a]	Neutron bombardment	45
238–352	$0.24 \exp[-(1600 \pm 90/RT)]$	F_2 + CD_4/C_2H_6	74
	(1) F + C_3H_8 → FH + $CH_3CH_2CH_2$; (2) F + *n*-C_4H_{10} → $CH_3CHCH_2CH_3$		
293–348	$2.81 \pm 0.05 \exp[-(130 \pm 120)/RT]$	Competitive method F_2 + hydrocarbons	72
	(1) F + CH_2D_2 → FH + CHD_2; (2) F + CH_2D_2 → FD + CH_2D		
159–298	$(0.81 \pm 0.03) \exp[(275 \pm 15)/RT]$	Microwave discharge SF_6	154

[a] These ratios, although not presented in the original reference, have been calculated from other ratios given in the reference.

TABLE XV. Arrhenius Parameters for Reaction with Saturated Hydrocarbons

Temp, K	E, kcal mol^{-1}	Log A, cm^3 mol^{-1} s^{-1}	Method	Ref
$F + CH \rightarrow FH + C$				
1000–4000	$k = 3.0 \times 10^{11} T^{0.68} \exp(-1000/RT)$		(Estimate)	89
298–2500	$k = 1.0 \times 10^{11} T^{0.67} \exp(-1800/RT)$		(Estimate)	90
1000–4000	$k = 1.0 \times 10^{11} T^{0.67} \exp(-4300/RT)$		(Estimate)	192
$F + CH_3 \rightarrow$ products				
250–400	$k < 3 \times 10^{13}$		$NF_2 + N$	19
$F + CH_4 \rightarrow FH + CH_3$				
178–373	1.210	13.39	F_2 + hydrocarbon	9
	$k \geqslant 6 \times 10^{13}$		Microwave discharge F_2	44
250–400	1.150	14.52	$N + NF_2$	19
178–373	1.210	14.00	F_2 + hydrocarbons	152
	3		(Estimate)	96
	1.850 ± 0.230	13.60	Competitive method. F_2 + hydrocarbons	72
298	$k > 5 \times 10^{12}$		(Estimate)	153
~300	$k = 4.3 \times 10^{13}$		Flash photolysis WF_6 HF chemical laser	49
298	$k = 3.6 \times 10^{13}$		Microwave discharge CF_4	31
$F + CD_4 \rightarrow FD + CD_3$				
	2.080	13.57	F_2 + hydrocarbons	74
$F + C_2H_6 \rightarrow FH + C_2H_5$				
178–373	0.280	12.90	F_2 + hydrocarbons	9
178–373	0.220	13.43	(Estimate)	19
178–373	0.280	13.70	F_2 + hydrocarbons	152
	2		(Estimate)	96
	0.480 ± 0.020	13.00	Competitive method F_2 + hydrocarbons	72
298	$k > 5 \times 10^{12}$		(Estimate)	153
$F + C_3H_8 \rightarrow FH + CH_3CH_2CH_2$				
178–373	0	12.64	F_2 + hydrocarbons	9
178–373	−0.060	13.18	(Estimate)	19
178–373	0	13.4	F_2 + hydrocarbons	152
	2		(Estimate)	96
	0.010 ± 0.010	13.70	Competitive method F_2 + hydrocarbons	72
$F + C_3H_8 \rightarrow FH + (CH_3)_2CH$				
178–373	0	12.71	F_2 + hydrocarbons	9
178–373	−0.060	13.20	(Estimate)	19
178–373	0	13.0	F_2 + hydrocarbons	152
$F + n\text{-}C_4H_{10} \rightarrow FH + CH_3CH_2CH_2CH_2$				
178–373	0	12.59	F_2 + hydrocarbon	9
178–373	−0.060	13.11	(Estimate)	19
178–373	0	13.3	F_2 + hydrocarbon	152
	0.010 ± 0.010	13.70	Competitive method F_2 + hydrocarbon	72
$F + n\text{-}C_4H_{10} \rightarrow FH + CH_3CHCH_2CH_3$				
178–373	0	12.67	F_2 + hydrocarbon	9
178–373	−0.060	13.00	(Estimate)	19
178–373	0	13.3	F_2 + hydrocarbon	152
$F + i\text{-}C_4H_{10} \rightarrow FH + CH_3CH(CH_3)CH_2$				
178–373	0	12.61	F_2 + hydrocarbon	9
178–373	−0.060	13.11	(Estimate)	19
178–373	0	13.6	F_2 + hydrocarbon	152
$F + i\text{-}C_4H_{10} \rightarrow FH + (CH_3)_3C$				
178–373	0	12.76	F_2 + hydrocarbon	9
178–373	−0.060	13.28	(Estimate)	19
178–373	0	12.8	F_2 + hydrocarbon	152
	2		(Estimate)	96
$F + neo\text{-}C_5H_{12} \rightarrow FH + CH_3(CH_2)_3CH_2$				
178–373	0	12.58	F_2 + hydrocarbon	9
178–373	−0.060	13.11	(Estimate)	19
178–373	0	13.7	F_2 + hydrocarbon	152
$F + c\text{-}C_3H_6 \rightarrow FH + c\text{-}C_3H_5$				
178–373	0	12.59	F_2 + hydrocarbon	9
178–373	−0.060	13.23	(Estimate)	19
178–373	0	13.4	F_2 + hydrocarbon	152

Abstraction of the hydroxyl hydrogen did not occur, as no ESR spectrum of the CH_3O radical could be detected.

A complete summary of the Arrhenius parameters which have been published for the reactions of fluorine atoms with saturated hydrocarbons appears in Table XV.

B. Reaction with Unsaturated Hydrocarbons

Whereas F atoms usually abstract hydrogen from saturated hydrocarbons, the reaction with unsaturated hydrocarbons involves either abstraction of hydrogen or addition of F to the multiple bond.

The reaction of F atoms with ethylene has not been studied to any great extent. A major problem in determining the products of the reaction is that one product formed is acetylene, which in turn reacts with F atoms.[82,153] Wolfrum[153] estimated a lower limit of 5×10^{12} $cm^3\ mol^{-1}\ s^{-1}$ for the rate constant for the overall reaction of F atoms with C_2H_4.

Parson and Lee[156] using crossed molecular beams of F atoms and C_2H_4 or C_2D_4 studied the angular distributions of both substitution and abstraction reaction products for the reactions $F + C_2H_4$, C_2D_4 using a mass spectrometric universal detector. The addition intermediate was said to be a long-lived complex, $C_2H_4F^{\ddagger}$, which eventually released a hydrogen atom and C_2H_3F. Zetzsch[47] found the mass spectrum of the products of the $F + C_2H_4$ reaction to include mass peaks for C_2H_6, C_2H_2, C_2H_3F, $C_2H_2F_2$, C_2HF_3, and C_4H_{10}. The following reactions were considered possible:

$$F + C_2H_4 \rightarrow C_2H_3F + H \qquad (186)$$

$$F + C_2H_4 \rightarrow C_2H_4F \qquad (187)$$

$$F + C_2H_4F \rightarrow CH_3 + CHF_2 \qquad (188)$$

$$F + C_2H_4F \rightarrow 2CH_2F \qquad (189)$$

The reaction of F atoms with acetylene is more clearly understood. Williams and Rowland[45,78] were able to compare the rate constant for abstraction of a hydrogen atom from C_2H_2 to the rate constant for F atom addition to C_2H_2. The ratio $k_{\text{abstraction}}/k_{\text{addition}}$ was about 0.13. Kapralova et al.,[157] in a study of the reaction of molecular fluorine with C_2H_2, described the rate of addition of F atoms to C_2H_2 as "very fast". The rate constant was found to be about 10^{13} $cm^3\ mol^{-1}\ s^{-1}$ by Zetzsch,[47] who proposed the following mechanism:

$$F + C_2H_2 \rightleftarrows C_2H_2F \qquad (190)$$

$$F + C_2H_2F \rightarrow C_2H_2F_2^* \qquad (191)$$

$$C_2H_2F_2^* + M \rightarrow C_2H_2F_2 + M \qquad (192)$$

$$C_2H_2F_2^* \rightarrow C_2HF + HF \qquad (193)$$

Wolfrum,[153] using a mass spectrometer to measure the decrease in acetylene concentration, found for the abstraction reaction

$$F + C_2H_2 \rightarrow C_2H + HF \qquad (194)$$

that $k_{194} = (3.5 \pm 1.0) \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ at room temperature. The C_2H dimerized to form C_4H_2. Cochran et al.[155] studied the reaction of $F + C_2D_2$ in a matrix and found evidence of the addition product $CD{=}CDF$, but were not positive that the deuterium abstraction product, $C{\equiv}CD$, formed.

The reactions of F atoms with higher unsaturated hydrocarbons have been studied by Shobatake et al.,[158] Parson et al.,[159] Williams et al.,[160] and Bumgardner et al.[41,161] From crossed molecular beam studies, the reactions of F atoms with monoolefins, cycloolefins, and dienes were found to form addition complexes which decompose unimolecularly to give predominantly H atoms or methyl radicals.[158] For a series of butene isomers, it was found that the group most distant from the C–F bond in the complex was most likely to be split off.[159]

TABLE XVI. Products of the Reaction of F Atoms with Unsaturated Hydrocarbons with $C > 3$

Reactant	Product	Ref
Isoprene	$FHC{=}C(CH_3)CH{=}CH_2 + H$ $H_2C{=}CFCH{=}CH_2 + CH_3$ $H_2C{=}CFCH_3 + CH_2{=}CH$	158
1,4-Pentadiene	$FHC{=}CHCH_2CH{=}CH_2 + H$ $FH_2CCH{=}CHCH{=}CH_2 + H$ $FCH_2CH{=}CH_2 + CH_2{=}CH$ $FCH{=}CH_2 + CH_2{=}CHCH_2$	158
1,3-Pentadiene	$FHC{=}CHCH{=}CHCH_3 + H$ $FH_2CCH{=}CHCH{=}CH_2 + H$ $FHC(CH{=}CH_2)_2 + H$ $FHC{=}CHCH{=}CH_2 + CH_3$ $FH_2CCH{=}CH_2$	158
1–5 Hexadiene	$FHC{=}CHCH_2CH_2CH{=}CH_2 + H$ $FH_2CCH{=}CH{-}CH_2CH{=}CH_2 + H$ $FH_2CCH{=}CH_2 + CH_2{=}CHCH_2$	158
Cyclohexene	2-Fluorocyclohex-1-ene + H 3-Fluorocyclohex-1-ene + H	158
$(H_3C)_2C{=}C(CH_3)_2$	$(H_3C)_2CFC(CH_3){=}CH_2 + H$	158
$(H_3C)_2C{=}C(CH_2)_2$	$(H_3C)_2C{=}CFCH_3 + CH_3$	158
$(H_3C)_2C{=}CHCH_3$	$(H_3C)_2C{=}CFCH_3 + H$ $H_3C{=}CFC(CH_3){=}CH_2 + H$ $(H_3C)_2CFCH{=}CH_2 + H$	158
$(H_3C)_2C{=}CHCH_3$	*cis*·$CH_3CF{=}CHCH_3 + CH_3$ *trans*-$CH_3CF{=}CHCH_3 + CH_3$ $(CH_3)_2C{=}CHF + CH_3$	158
trans-3-Hexene	$H_2C{=}CHCHFC_2H_5 + CH_3$ $H_3CCH_2CH{=}CFC_2H_5 + H$ $H_3CCH{=}CHCHFC_2H_5 + H$ $H_2C{=}CHCHFC_2H_5 + CH_3$ $FHC{=}CHCH_2CH_3 + C_2H_5$	158
cis·2-Butene	*cis*- and *trans*·$H_3CCH{=}CHF + CH_3$ $H_3CCHFCH{=}CH_2 + H$ *cis*- and *trans*-$H_3CCH{=}CFCH_3 + H$	159
trans-2-Butene	*cis*- and *trans*-$H_3CCH{=}CHF + CH_3$ $H_3CCHFCH{=}CH_2 + H$ *cis*- and *trans*-$H_3CCH{=}CFCH_3 + H$	159
Isobutene	$H_2C{=}CFCH_3 + CH_3$ $HFC{=}C(CH_3)_2 + H$ $FH_2CC(CH_3){=}CH_2 + H$	159
1-Butene	$FH_2CCH{=}CH_2 + CH_3$ *cis*· and *trans*- $H_3CCH_2CH{=}CHF + H$ *cis*· and *trans*- $FH_2CCH{=}CHCH_3 + H$ *cis*· and *trans*- $H_3CCH_2CF{=}CH_2 + H$	159

A list of products observed from the reaction of F atoms with a number of monoolefins, cycloolefins, and dienes is given in Table XVI.

Williams et al.[160] found that F atoms reacted with propylene according to the reactions

$$F + CH_3CH{=}CH_2 \rightarrow CH_3CHCH_2F^* \qquad (195)$$

$$F + CH_3CH{=}CH_2 \rightarrow CH_3CHF{=}CH_2^* \qquad (196)$$

The value of 1.35 for the ratio k_{195}/k_{196} found by Williams et al. differed markedly from the value of 3.0 found by Bumgardner et al. Williams et al. suggested that the higher value was caused by excessive loss of

$$CH_3CHF{=}CH_2^* \rightarrow CH_3 + CH_2{=}CHF \qquad (197)$$

at the lower pressures (150 Torr) used by Bumgardner et al. Williams et al. found that 20% of these radicals decomposed at 400 Torr.

Bumgardner et al.[161] found a value of 1.0 for $k_{198}/(k_{195} + k_{196})$.

TABLE XVII. Absolute and Relative Rate Constants for Reaction with Unsaturated Hydrocarbons

Temp, K	k, cm^3 mol^{-1} s^{-1}	Method	Ref
$F + C_2H_4 \rightarrow$ products			
298	$>5 \times 10^{12}$	(Estimate)	153
$F + C_2H_2 \rightarrow FH + C_2H$			
298	$(3.5 \pm 1.0) \times 10^{12}$	Microwave discharge CF_4	153
$F + C_2H_2 \rightarrow C_2H_2F$			
298	$\sim 10^{13}$	Microwave discharge CF_4	47
(1) $F + C_2H_2 \rightarrow FH + C_2H$; (2) $F + C_2H_2 \rightarrow CHFCH$			
283	$k_1/k_2 = 0.12 \pm 0.02$	Neutron bombardment	45
283	$k_1/k_2 = 0.14 \pm 0.07$	Neutron bombardment	78
(1) $F + CH_3CH{=}CH_2 \rightarrow CH_3CHCH_2F^*$; (2) $F + CH_3CH{=}CH_2 \rightarrow CH_3CHFCH_2^*$			
	$k_1/k_2 = 1.35$	Neutron bombardment	160
	$k_1/k_2 = 3.0$	Photochemical reaction NF_2	161
(1) $F + CH_3CH{=}CH_2 \rightarrow FH + CH_2CH{=}CH_2$; (2) $F + CH_3CH{=}CH_2 \rightarrow$ addition products			
	$k_1/k_2 = 1.0$	Photochemical reaction NF_2	161
(1) $F + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_2CCH_2F$; (2) $F + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_2CFCH_2$			
	$k_1/k_2 = 3.1$	Photochemical reaction NF_2	161
(1) $F + (CH_3)_2C{=}CH_2 \rightarrow FH + CH_3C(CH_2){=}CH_2$: (2) $F + (CH_3)_2C{=}CH_2 \rightarrow$ addition products			
	$k_1/k_2 = 1.2$	Photochemical reaction NF_2	161
(1) $F + C_6H_6 \rightarrow C_6H_6$; (2) $F + C_2H_2 \rightarrow C_2H_2F$			
	$k_1/k_2 = 1.5 \pm 0.5$	Neutron bombardment	166

$$F + CH_3CH{=}CH_2 \rightarrow HF + CH_2CH{=}CH_2 \qquad (198)$$

They obtained similar results for isobutylene, with a ratio of abstraction to addition of 1.2, and a ratio of terminal to central addition of 3.1.

Bumgardner and Lawton[41] found that F atoms react with methylacetylene to give both central and terminal addition and abstraction products

$$F + CH_3C{\equiv}CH \rightarrow HF + CH_2C{\equiv}CH \qquad (199)$$

$$F + CH_3C{\equiv}CH \rightarrow CH_3C{=}CFH \qquad (200)$$

$$F + CH_3C{\equiv}CH \rightarrow CH_3CF{=}CH \qquad (201)$$

The F atom/allene reaction produced only abstraction and central addition products. The terminal addition product may have been lost through rearrangement.

$$F + CH_2{=}C{=}CH_2 \rightarrow HF + CH{=}C{=}CH_2 \qquad (202)$$

$$F + CH_2{=}C{=}CH_2 \rightarrow CH_2{=}CFCH_2 \qquad (203)$$

A complete summary of the absolute and relative rate constants of the reaction of F atoms with unsaturated hydrocarbons is given in Table XVII.

C. Reaction with Aromatic Hydrocarbons

There have been virtually no kinetic studies on the reaction of F atoms with aromatic hydrocarbons. However, four research groups have studied some F atom/aromatic systems.

TABLE XVIII. Reaction of F Atoms with Aromatic Hydrocarbons and Heterocyclic Compounds[a]

Reactant		Products
C_6H_5D	→	$C_6H_5F + D$ $C_6H_4DF + H$
$C_6H_5CH_3$	→	$C_6H_4FCH_3 + H$ $C_6H_5F + CH_3$
m-$C_6H_4(CH_3)_2$	→	$C_6H_3(CH_3)_2F + H$ $C_6H_4(CH_3)F + CH_3$
Cycloheptatriene (C_7H_8)	→	$C_7H_7F + H$ $C_6H_5F + CH_3$
Thiophene	→	F-thiophene + H
Furan	→	F-furan + H
Pyridine	→	F-pyridine + H
C_6H_5Cl	→	$C_6H_4FCl + H$ $C_6H_5F + Cl$

[a] Compiled from ref 163.

Cochran et al.[155] used ESR to study the products of the photolytic reaction of F atoms with perdeuterated benzene. The addition product was definitely confirmed:

$$F + C_6D_6 \rightarrow C_6D_6F \qquad (204)$$

The deuterated phenyl radical C_6D_5 was also observed, but it was unknown whether it was produced by abstraction as in reaction 205 or by secondary photolysis of C_6D_6F.

$$F + C_6D_6 \rightarrow C_6D_5 + DF \qquad (205)$$

Shobatake et al.[162,163] studied the reactions of F atoms with various aromatic and heterocyclic compounds by the crossed molecular beam technique. The reactions all proceeded through a long-lived intermediate complex before emitting an H atom or free radical. A list of the reactions thus studied appears in Table XVIII.

Vasek and Sams[164,165] reported that the reaction of F atoms with bromobenzene produced the three bromofluorobenzenes, the yield decreasing in the order: para > ortho > meta. Reaction with fluorobenzene indicated that an F atom in the ring had a greater inhibiting effect on substitution in the ortho position than did a bromine atom. The yield of difluorobenzene followed the pattern: para ≫ ortho ≈ meta.

Cramer and Rowland[166] have analyzed the products of the reaction of thermal ^{18}F atoms with benzene and various substituted benzenes. The reaction with benzene produced only fluorobenzene as a radiodetectable product. Addition of oxygen to the mixture increased the fluorobenzene yield, possibly by the process

$$C_6H_6{}^{18}F + O_2 \rightarrow C_6H_5{}^{18}F + HO_2 \qquad (206)$$

Reaction of ^{18}F with fluorobenzene produced the three difluorobenzenes in the ratio, para:ortho:meta = 3.4:2.6:1.1. Addition of O_2 enhanced the *para* and *meta* yields and depressed the *ortho* yield. Reaction of ^{18}F with *m*-difluorobenzene produced the three trifluorobenzenes in the ratio, 1,2,4-$C_6H_3F_3$:1,2,3-$C_6H_3F_3$:1,3,5-$C_6H_3F_3$ = 2.7:0.48:0.38. Addition of O_2 greatly increased the production of 1,3,5-$C_6H_3F_3$, since this was the only form where no two F atoms were ortho to each other. Reaction of ^{18}F with trifluoromethylbenzene produced the three trifluoromethylfluorobenzenes in the order meta > para ≫ ortho. The addition of oxygen increased all three yields: thus there was no "negative ortho" effect. They reported the reaction of ^{18}F atoms with C_6H_6 to be 1.5 ± 0.5 times as fast as the reaction with C_2H_2.

D. Reaction with Halogen-Substituted Hydrocarbons

1. Fluorine Substitution Only

Rate constants and/or activation energies have been found for reactions of F atoms with CHF_3,[31,44,47,96] CH_2F_2,[13,44] and CH_3F.[13,44] In each case, the F atom abstracts an H atom

$$F + CH_xF_{4-x} \rightarrow HF + CH_{x-1}F_{4-x} \qquad (207)$$

Fettis et al.[152] found that reaction of F atoms with CH_3F proceeds at nearly the same rate as the reaction of F atoms with CH_3Cl or CH_3Br, while chlorination or bromination of CH_3F would be much slower than chlorination or bromination of CH_3Cl or CH_3Br.

Modica[167] and Modica and Sillers[168] found the rate constants for F attack on CF, CF_2, CF_3, and CF_4 in shock tubes by following the concentration of CF_2 by its absorption at 260 nm.

Fredricks and Tedder reported on the reactions of F atoms with *n*-butyl fluoride[169] and 2-fluorobutane.[170] In both reactions, they found an H atom to be replaced by an F atom. It was found that the presence of an F atom on the hydrocarbon retarded attack on the adjacent carbon atoms, and correspondingly increased the possibility of attack on the most distant carbon atoms.

Bumgardner and Lawton[41] found the reaction of F with $CH_2{=}CF_2$ resulted in the production of CF_3CH_2 and CF_2CH_2F in the ratio of 2.3 to 1. This was unusual but was explained as being due either to pressure effects, or to F atom migration.

2. Chlorine Substitution Only

Studies of the reaction of F atoms with CCl_4 have given the widest range of inconsistent results of any F atom reaction. There are two possible initiation steps:

$$F + CCl_4 \rightarrow CCl_3 + FCl \qquad (208)$$

$$F + CCl_4 \rightarrow CCl_3F + Cl \qquad (209)$$

Reaction 208 is 8.8 kcal mol^{-1} endothermic while reaction 209 is 36 kcal mol^{-1} exothermic.[171] Using molecular fluorine and CCl_4 in N_2, Clark and Tedder[11] arrived at a rate constant for reaction 208 of 2×10^{13} cm^3 mol^{-1} s^{-1} at room temperature. They postulated the following mechanism

$$F_2 \rightarrow 2F \qquad (210)$$

$$F + CCl_4 \rightarrow CCl_3 + FCl \qquad (208)$$

$$CCl_3 + F_2 \rightarrow CCl_3F + F \qquad (211)$$

$$F + F \rightarrow F_2 \qquad (212)$$

The rate constant, 2×10^{13} cm^3 mol^{-1} s^{-1}, was later disputed by Kaufman and co-workers[28,171,172] who contended that Clark and Tedder were unable to accurately measure F atom concentration because of chain branching. Kaufman's group, by mass spectrometric molecular beam analysis, arrived at a rate constant of 2.4×10^8 cm^3 mol^{-1} s^{-1} for reaction 208. This reaction was taken as the initiating step, as mass spectral analysis showed no $CFCl_3$ present, eliminating reaction 209. Chlorine atoms were observed, but these were attributed to the chain-branching reaction

$$F + CCl_3 \rightarrow FCCl_2 + Cl \qquad (213)$$

Foon and Tait[173] followed the reaction of F_2 with CCl_4 by measuring the buildup of CCl_3F (reaction 211). They also measured the rate constant for the rate-determining step, $k_{208} = 6.92 \times 10^5$ cm^3 mol^{-1} s^{-1}. There is obviously much discrepancy over the actual rate constant for reaction 208.

The reaction of F atoms with partially chlorinated methanes, CH_xCl_{4-x}, have been studied by Fettis et al.,[152] Wagner et al.,[19] Foon and co-workers,[13,72,74] and Clyne et al.[31] Upon reaction with F atoms the chloromethanes, like their fluorine counterparts, all have a hydrogen atom abstracted.

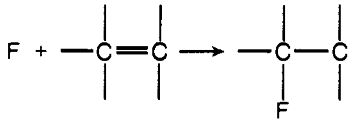
$$F + CH_xCl_{4-x} \rightarrow HF + CH_{x-1}Cl_{4-x} \qquad (214)$$

The activation energies for the reaction of F atoms with the series of chloromethanes pass through a minimum at CH_2Cl_2,[13] which is partially due to the corresponding minimum in C–H bond strength with CH_2Cl_2. Foon and co-workers,[13,72] Fettis et al.,[152] and Wagner et al.[19] measured k_{214} for each chloromethane relative to each other and relative to the reaction of F atoms with hydrocarbons. The results of Fettis et al.[152] are probably incorrect owing to self-heating errors.[13] Absolute rate constants k_{214} were calculated from previous data for *n*-butane[13] and methane[19] or from assumed values for ethane.[72] Clyne and co-workers[31] obtained absolute rate constants for reaction 214 from direct mass spectral sampling, but the values were only accurate to ±25%. At room temperature, k_{214} is about 10^{12}–10^{13} cm^3 mol^{-1} s^{-1} for all chloromethanes.

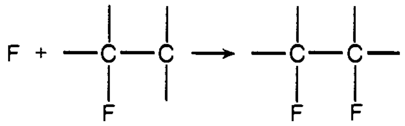
Foon et al.[74] reported that the isotope effect observed for the reaction of F atoms with $CHCl_3$ and $CDCl_3$ was due mainly to the 0.6 kcal mol^{-1} higher activation energy of the deuterated chloroform.

Fredricks and Tedder[169,170] studied the attack of F atoms on *n*-butyl chloride and 2-chlorobutane. The presence of chlorine greatly retarded fluorine attack on adjacent carbon atoms and eliminated attack entirely on the carbon atom occupied by the chlorine.

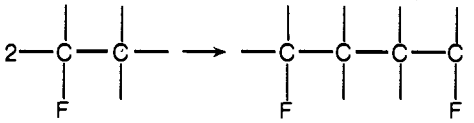
Miller and Koch[174] showed that the reaction of perhaloolefins with fluorine atoms leads to dimerization as follows:



$$F + -\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}- \rightarrow -\overset{|}{\underset{\underset{F}{|}}{C}}-\overset{|}{\underset{|}{C}} \qquad (215)$$



$$F + -\overset{|}{\underset{\underset{F}{|}}{C}}-\overset{|}{\underset{|}{C}} \rightarrow -\overset{|}{\underset{\underset{F}{|}}{C}}-\overset{|}{\underset{\underset{F}{|}}{C}}- \qquad (216)$$



$$2-\overset{|}{\underset{\underset{F}{|}}{C}}-\overset{|}{\underset{|}{C}}- \rightarrow -\overset{|}{\underset{\underset{F}{|}}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{F}{|}}{C}} \qquad (217)$$

However, the presence of hydrogen in trichloroethylene allows an abstraction reaction to occur:[175]

$$F + CHCl{=}CCl_2 \rightarrow CCl_2{=}CCl + HF \qquad (218)$$

3. Fluorine and Chlorine Substitution

The reaction of F atoms with compounds of the series CF_xCl_{4-x} results in abstraction of a Cl atom at room temperature and replacement of a Cl atom at flame temperatures. The reaction was studied by Foon and Tait[173,176,177] at temperatures up to 750 K in the presence of molecular fluorine. They postulated the following mechanism

$$F_2 + M \rightarrow 2F + M \qquad (219)$$

$$F + RCl \rightleftarrows FCl + R \qquad (220)$$

$$F + F_2 \rightarrow RF + F \qquad (221)$$

$$R + FCl \rightarrow RF + Cl \qquad (222)$$

$$Cl + F_2 \rightarrow FCl + F \qquad (223)$$

$$F + F + M \rightarrow F_2 + M \qquad (224)$$

where R = CF_3, CF_2Cl, or $CFCl_2$.

Zetzsch[47] reported that the abstraction reactions are quite slow at 300 K, having a rate constant of about 10^9 cm^3 mol^{-1} s^{-1}. Foon and Tait[173] showed that both the activation energy and frequency factors for the reactions with CF_xCl_{4-x} increases with increasing *x*, with the exception that the value of the frequency factor for the reaction F + CCl_4 lies intermediate in the series.

TABLE XIX. Reaction with Halogen-Substituted Hydrocarbons

Temp, K	k, cm^3 mol^{-1} s^{-1}	Method	Ref
	$F + CHF_3 \rightarrow FH + CF_3$		
301–667	$1.05 \times 10^{12} \exp[-(2.38 \pm 0.75) \times 10^3/RT]$	Microwave discharge F_2	31
274–354	$7.5 \times 10^{12} \exp(-2.2 \times 10^3/RT)$	Microwave discharge CF_4	47
	1.9×10^{11}	Microwave discharge F_2	44
	$E \approx 3$ kcal mol^{-1}	(Estimate)	96
	$F + CH_2F_2 \rightarrow FH + CHF_2$		
	1.1×10^{13}	Microwave discharge F_2	44
	$E = 2.4$ kcal mol^{-1}		*a*
	$F + CH_3F \rightarrow FH + CH_2F$		
	5.3×10^{13}	Microwave discharge F_2	44
	$E = 1.07$ kcal mol^{-1}		*a*
	$F + CF_4 \rightarrow CF_3 + F_2$		
1700–3000	$1.00 \times 10^{12} T^{0.5} \exp(-85.63 \times 10^3/RT)$	(Estimate)	168
	$F + CF_3 \rightarrow CF_2 + F_2$		
1700–3000	$1.00 \times 10^{12} T^{0.5} \exp(-55.60 \times 10^3/RT)$	(Estimate)	168
	$F + CF_3 + Ar \rightarrow CF_4 + Ar$		
1700–3000	$9.79 \times 10^{31} T^{-4.64} \exp(-2.849 \times 10^3/RT)$ cm^6 mol^{-1} s^{-1}	(Estimate)	168
	$F + CF_2 + Ar \rightarrow CF_3 + Ar$		
1700–3000	$1.49 \times 10^{46} T^{-9.04} \exp(-2.287 \times 10^3/RT)$ cm^6 mol^{-2} s^{-1}	(Estimate)	168
	$F + CF + Ar \rightarrow CF_2 + Ar$		
2600–3500	$6.57 \times 10^{26} T^{-2.85}$ cm^6 mol^{-2} s^{-1}	(Estimate)	167
	$F + CCl_4 \rightarrow FCl + CCl_3$		
293	2×10^{13}	$F_2 + CCl_4$	11
298	2.4×10^8	Microwave discharge F_2 or CF_4	28, 171
293	6.92×10^5	$F_2 + CCl_4$	173
399–498	$1 \times 10^{13} \exp[-(10.2 \pm 0.1) \times 10^3/RT]$	$F_2 + CCl_4$	173
300	$\leq 5 \times 10^{10}$	Microwave discharge CF_4	47
	$F + CCl_3F \rightarrow FCl + CCl_2F$		
~530	$3 \times 10^{12} \exp[-(13.1 \pm 0.1) \times 10^3/RT]$	Competitive F_2 + halocarbons	173
300	$\sim 1 \times 10^9$	Microwave discharge CF_4	47
	$F + CCl_2F_2 \rightarrow FCl + CClF_2$		
~674	$1.5 \times 10^{13} \exp[-(16.7 \pm 0.3) \times 10^3/RT]$	Competitive F_2 + halocarbons	173
300	$\sim 1 \times 10^9$	Microwave discharge CF_4	47
	$F + CF_3Cl \rightarrow FCl + CF_3$		
~765	$6 \times 10^{13} \exp[-(20.9 \pm 0.7) \times 10^3/RT]$	Competitive F_2 + halocarbons	173
300	$\sim 1 \times 10^9$	Microwave discharge CF_4	47
	$F + CClF_2CF_2Cl \rightarrow FCl + CClF_2CF_2$		
~673	$1.5 \times 10^{13} \exp[-(18.2 \pm 0.3) \times 10^3/RT]$	Competitive F_2 + halocarbons	173
	$F + CF_3CF_2Cl \rightarrow FCl + CF_3CF_2$		
~735	$6 \times 10^{12} \exp[-(18.4 \pm 0.3) \times 10^3/RT]$	Competitive F_2 + halocarbon	173
	$F + CH_3Cl \rightarrow FH + CH_2Cl$		
209–291	$1.18 \times 10^{13} \exp[-1.07 \times 10^3/RT]$	Competitive F_2 + halocarbon	13
	$3.2 \times 10^{13} \exp[-1.01 \times 10^3/RT]$	(Estimate)	19
250–348	$(1.27 \pm 0.05) \times 10^{13} \exp[-(1.08 \pm 0.08) \times 10^3/RT]$	Competitive F_2 + compounds	72
298	$(1.56 \pm 30\%) \times 10^{13}$	Microwave discharge F_2	31
	$F + CH_2Cl_2 \rightarrow FH + CHCl_2$		
250–353	$2.2 \times 10^{12} \exp[-(0.124 \text{ to } 0.210) \times 10^3/RT]$	Competitive F_2 + halocarbon	13
	$3.9 \times 10^{12} \exp[-0.100 \times 10^3/RT]$	(Estimate)	19
298	$(5.8 \pm 25\%) \times 10^{12}$	Microwave discharge F_2	31
	$F + CHCl_3 \rightarrow FH + CCl_3$		
250–348	$3.1 \times 10^{12} \exp[-(0.621 \text{ to } 0.707) \times 10^3/RT]$	Competitive F_2 + halocarbon	13
	$8.4 \times 10^{12} \exp[-0.600 \times 10^3/RT]$	(Estimate)	19
298	$(3.2 \pm 25\%) \times 10^{12}$	Microwave discharge F_2	31

TABLE XIX (Continued)

Temp, K	k, cm^3 mol^{-1} s^{-1}	Method	Ref
	$F + CHCl_2F \rightarrow FH + CCl_2F$		
250–348	$1.25 \times 10^{13} \exp[-(1.29 \text{ to } 1.37) \times 10^3/RT]$	Competitive F_2 + halocarbon	13
	$3.4 \times 10^{13} \exp[-1.28 \times 10^3/RT]$	(Estimate)	19
	$F + CHClF_2 \rightarrow FH + CClF_2$		
250–353	$4.7 \times 10^{12} \exp[-(1.27 \pm 1.37) \times 10^3/RT]$	Competitive F_2 + halocarbon	13
	$1.3 \times 10^{13} \exp[-1.26 \times 10^3/RT]$	(Estimate)	19
298	1.5×10^{12}	Microwave discharge F_2	44
	$F + CDCl_3 \rightarrow FD + CCl_3$		
250–346	$(3.8 \pm 1.0) \times 10^{12} \exp[-(1.28 \pm 0.05) \times 10^3/RT]$	Calculation from competitive method	74
	$F + CF_3Br \rightarrow$ products		
298	4×10^9	Microwave discharge F_2	44
296	$(5.7 \pm 2) \times 10^8$	Microwave discharge F_2 or CF_4	186
	$F + CF_3Br + M \rightarrow CF_3BrF + M$		
296	2.4×10^{17} cm^6 mol^{-2} s^{-1}	Microwave discharge F_2 or CF_4	184
296	1.8×10^{17} cm^6 mol^{-2} s^{-1}	Microwave discharge F_2 or CF_4	186
298	2.6×10^{17} cm^6 mol^{-2} s^{-1}	Microwave discharge F_2 or CF_4	185
	$F + CCl_3Br \rightarrow FBr + CCl_3$		
298	$(5.6 \pm 2.2) \times 10^{13}$, $E \approx 0$ kcal mol^{-1}	Microwave discharge F_2	182, 183
	$F + CF_3I \rightarrow FI + CF_3$		
298	$(7.2 \pm 3) \times 10^{13}$, $E \approx 0$ kcal mol^{-1}	Microwave discharge F_2	182, 183
298	$(1.02 \pm 0.36) \times 10^{14}$	Discharge F_2	187
	$F + CH_3I \rightarrow$ products (FH, CH_2I, FI, CH_3)		
298	$(1.2 \pm 0.4) \times 10^{14}$	Discharge F_2	187

[a] N. A. McAskill, M.Sc. Thesis, University of New South Wales, 1966, as quoted in ref 13.

MacLean[83] and Homann and MacLean[178,179] found that, in a fluorine/halocarbon flame, chlorine atom replacement occurs as follows:

$$F + CF_xCl_{4-x} \rightarrow CF_{x+1}Cl_{4-x-1} + Cl \quad (225)$$

No compounds containing more than one carbon atom were found, indicating that radicals of the type CF_3, CF_2Cl, etc., were not formed in the reaction. The mechanism for a F_2/CF_2Cl_2 flame was reported as

$$F + CCl_2F_2 \rightarrow CClF_3 + Cl \quad (226)$$

$$Cl + F_2 \rightarrow FCl + F \quad (223)$$

$$F + CClF_3 \rightarrow CF_4 + Cl \quad (227)$$

$$FCl + Cl \rightarrow Cl_2 + F \quad (228)$$

At 1600 K, the ratio k_{226}/k_{227} was reported to be 7.[83]

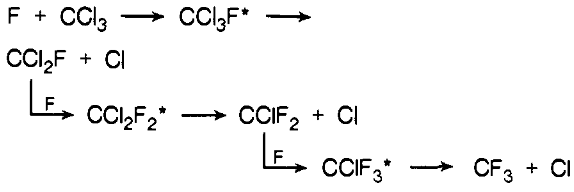
Rodgers studied the reactions of atomic fluorine with 2,3-dichloroperfluorobutene-2[180] and 1,4-dichloroperfluorobutene-2.[181] In each case, the fluorine adds to the double bond forming an activated complex which either expels a Cl atom or is deactivated by collision.

4. *Bromine-Containing Halocarbons*

Bozzelli and Kaufman[182,183] studied the reaction of atomic fluorine with CCl_3Br by molecular beam–mass spectrometric analysis and found the major pathway to be the abstraction reaction

$$F + CCl_3Br \rightarrow FBr + CCl_3 \quad (229)$$

with a rate constant of $k_{229} = (5.6 \pm 2.2) \times 10^{13}$ cm^3 mol^{-1} s^{-1} about 10^4 greater than the corresponding value for the reaction of F atoms with CCl_3F. The reaction was found to be nonstoichiometric, which was attributed to the reaction of F atoms with the halocarbon radicals in a series of "atom-switching" reactions.



$$F + CCl_3 \rightarrow CCl_3F^* \rightarrow CCl_2F + Cl$$
$$CCl_2F \xrightarrow{F} CCl_2F_2^* \rightarrow CClF_2 + Cl$$
$$CClF_2 \xrightarrow{F} CClF_3^* \rightarrow CF_3 + Cl \quad (230)$$

These reactions have nearly zero activation energy and rate constants of about 10^{13}–10^{14} cm^3 mol^{-1} s^{-1}.

Pollock and Jones[44] reported a rate constant of 4×10^9 cm^3 mol^{-1} s^{-1} for the reaction of F atoms with CF_3Br. Kaufman and co-workers[184,185] and Bozzelli[186] stated that the rate constant for this reaction was 10^8–10^9 cm^3 mol^{-1} s^{-1} and found that it decreased with increasing temperature, indicating a negative activation energy of −2.2 kcal mol^{-1}. Since no Br atoms were detected in the analysis, the authors proposed that displacement of Br by F was unlikely owing to a steric barrier. Since the abstraction of Br is endothermic and would not account for a negative activation energy, the mechanism postulated involves a pseudo-trihalogen radical intermediate as follows:

$$F + CF_3Br + M \rightarrow CF_3BrF + M \quad (231)$$

$$F + CF_3BrF \rightarrow CF_3Br + F_2 \quad (232)$$

$$F + CF_3BrF \rightarrow CF_3 + BrF_2 \quad (233)$$

The rate constant for reaction 231 was found to be between 1.8×10^{17} and 2.6×10^{17} cm^6 mol^{-2} s^{-1}. The ratio $k_{233}/k_{232} = 0.083$ was also determined at 296 K.

TABLE XX. Relative Rate Constants for Halogen-Substituted Hydrocarbons

Temp, K	k_1/k_2	Method	Ref
	(1) $F + CH_3F \rightarrow FH + CH_2F$; (2) $F + CH_4 \rightarrow FH + CH_3$		
	0.3	F_2 + compounds	152
	(1) $F + CH_3F \rightarrow FH + CH_2F$; (2) $F + CH_3Cl \rightarrow FH + CH_2Cl$		
	0.91[a]	F_2 + compounds	152
	(1) $F + CH_3F \rightarrow FH + CH_2F$; (2) $F + CH_3Br \rightarrow FH + CH_2Br$		
	1.30[a]	F_2 + compound	152
	(1) F + *n*-$C_4H_9F \rightarrow H + CH_2FCH_2CHFCH_3$; (2) F + *n*-$C_4H_9F \rightarrow H + CH_2FCH_2CH_2CH_2F$		
293	1.0	F_2 + *n*-butyl fluoride	169
	(1) F + *n*-$C_4H_9F \rightarrow H + CH_2FCHFCH_2CH_3$; (2) F + *n*-$C_4H_9F \rightarrow H + CH_2FCH_2CH_2CH_2F$		
293	0.8	F_2 + *n*-butyl fluoride	169
	(1) F + *n*-$C_4H_9F \rightarrow H + CHF_2CH_2CH_2CH_3$; (2) F + *n*-$C_4H_9F \rightarrow H + CH_2FCH_2CH_2CH_2F$		
203	<0.3	F_2 + *n*-butyl fluoride	169
	(1) $F + CH_3CF_3 \rightarrow FH + CH_2CF_3$; (2) $F + C_2H_2 \rightarrow CH_2FCH$		
283	0.05 ± 0.01	Neutron bombardment	45
283	0.053 ± 0.012	Neutron bombardment	78
	(1) $F + CH_3CF_3 \rightarrow FH + CH_2CF_3$; (2) $F + C_2H_6 \rightarrow FH + C_2H_5$		
283	0.042[a]	Neutron bombardment	45
283	0.038[a]	Neutron bombardment	78
	(1) $F + CCl_2F_2 \rightarrow CClF_3 + Cl$; (2) $F + CClF_3 \rightarrow CF_4 + Cl$		
1600	7	$F_2CCl_2F_2$ flame	83, 178
	(1) $F + CHCl_2F \rightarrow FH + CCl_2F$; (2) $F + CHClF_2 \rightarrow FH + CClF_2$		
250–338	2.66 ± 0.15	Competitive F_2 + halocarbons	13
	(1) $F + CH_3Cl \rightarrow FH + CH_2Cl$; (2) $F + CHCl_2F \rightarrow FH + CCl_2F$		
250–295	$(2.82 \pm 4.1) \exp[(0.210 \pm 0.490) \times 10^3/RT]$	Competitive F_2 + halocarbons	13
	(1) $F + CH_3Cl \rightarrow FH + CH_2Cl$; (2) $F + CH_2Cl \rightarrow FH + CHCl_2$		
250–333	$(7.91 \pm 3.53) \exp[-(0.860 \pm 0.250) \times 10^3/RT]$	Competitive F_2 + halocarbons	13
	4.7[a]	Competitive F_2 + halocarbons	*b*
	(1) $F + CH_2Cl_2 \rightarrow FH + CHCl_2$; (2) $F + CHClF_2 \rightarrow FH + CClF_2$		
273–353	$(0.95 \pm 0.13) \exp[(1.140 \pm 0.100) \times 10^3/RT]$	Competitive F_2 + halocarbons	13
	(1) $F + CH_2Cl_2 \rightarrow FH + CHCl_2$; (2) $F + CHCl_3 \rightarrow FH + CCl_3$		
250–326	$(1.44 \pm 0.25) \exp[(0.500 \pm 0.190) \times 10^3/RT]$	Competitive F_2 + halocarbons	13, 74
	0.12[a]	Competitive F_2 + halocarbons	*b*
	(1) $F + CHCl_3 \rightarrow FH + CCl_3$; (2) $F + CHCl_2F \rightarrow FH + CCl_2F$		
273–348	$(0.25 \pm 0.02) \exp[(0.670 \pm 0.080) \times 10^3/RT]$	Competitive F_2 + halocarbons	13
	(1) F + *n*-$C_4H_{10} \rightarrow FH + CH_3(CH_2)_2CH_2$; (2) $F + CH_3Cl \rightarrow FH + CH_2Cl$		
209–291	$(0.81 \pm 0.25) \exp[(1.070 \pm 0.160) \times 10^3/RT]$	Competitive F_2 + compounds	13
	(1) F + *neo*-$C_5H_{12} \rightarrow FH + CH_3(CH_2)_3CH_2$; (2) $F + CH_3Cl \rightarrow FH + CH_2Cl$		
293	7.7 ± 0.7	Competitive F_2 + compounds	13
	(1) $F + CH_3Cl \rightarrow FH + CH_2Cl$; (2) $F + CH_4 \rightarrow FH + CH_3$		
	0.33	Competitive F_2 + compounds	*b*
	(1) $F + CH_2Cl_2 \rightarrow FH + CHCl_2$; (2) $F + CH_4 \rightarrow FH + CH_3$		
	0.07	Competitive F_2 + compounds	*b*
	(1) $F + CHCl_3 \rightarrow FH + CCl_3$; (2) $F + CH_4 \rightarrow FH + CH_3$		
	0.6	Competitive F_2 + compounds	*b*
	(1) $F + CH_3Cl \rightarrow FH + CH_2Cl$; (2) $F + CHCl_3 \rightarrow FH + CCl_3$		
	0.55[a]	Competitive F_2 + halocarbons	*b*
	(1) $F + CH_3Cl \rightarrow FH + CH_2Cl$; (2) $F + C_2H_6 \rightarrow FH + C_2H_5$		
250–348	$(1.27 \pm 0.05) \exp[-(0.590 \pm 0.020) \times 10^3/RT]$	Competitive F_2 + compounds	72
	(1) $F + CH_3Cl \rightarrow FH + CH_2Cl$: (2) $F + C_3H_8 \rightarrow FH + CH_3CH_2CH_2$		
293–348	$(2.67 \pm 0.35) \exp[-(1.080 \pm 0.080) \times 10^3/RT]$	Competitive F_2 + compounds	72

TABLE XX (Continued)

Temp, K	k_1/k_2	Method	Ref
	(1) $F + CH_2Cl_2 \rightarrow FH + CHCl_2$; (2) $F + CDCl_3 \rightarrow FD + CCl_3$		
273–346	$(1.16 \pm 0.12) \exp[(1.12 \pm 0.06) \times 10^3/RT]$	Competitive F_2 + halocarbons	74
	(1) $F + CHCl_3 \rightarrow FH + CCl_3$; (2) $F + CDCl_3 \rightarrow FD + CCl_3$		
250–346	$(0.81 \pm 0.25) \exp[(0.62 \pm 0.20) \times 10^3/RT]$	Calculation from competitive results	74
	(1) $F + n\text{-}C_4H_9Cl \rightarrow H + CHClCH_2CHFCH_3$ and $CH_2ClCHFCH_2CH_3$; (2) $F + n\text{-}C_4H_9Cl \rightarrow H + CH_2Cl(CH_2)_2CH_2F$		
293	1.7	F_2 + *n*-butyl chloride	169
	(1) $F + CH_3Br \rightarrow FH + CH_2Br$; (2) $F + CH_4 \rightarrow FH + CH_3$		
	0.23	Competitive F_2 + compounds	*b*
	(1) $F + CH_3Br \rightarrow FH + CH_2Br$; (2) $F + CH_3Cl \rightarrow FH + CH_2Cl$		
	0.70[a]	Competitive F_2 + compounds	*b*
	(1) $F + CF_3BrF \rightarrow CF_3 + BrF_2$; (2) $F + CF_3BrF \rightarrow CF_3Br + F_2$		
296	0.083	Microwave discharge CF_4 or F_2	186

[a] These ratios, although not presented in the original reference, have been calculated from other ratios given in the reference. [b] R. Foon, as quoted in ref 152.

TABLE XXI. Reaction with Miscellaneous Substances

Reaction	Temp, K	k, $cm^3\ mol^{-1}\ s^{-1}$	Method	Ref
$F + AlH \rightarrow FH + Al$	298–2500	$9 \times 10^{10} T^{0.69} \exp[-5.6 \times 10^3/RT]$	(Estimate)	90
$F + BH \rightarrow FH + B$	298–2500	$1.6 \times 10^{11} T^{0.67} \exp[-3.6 \times 10^3/RT]$	(Estimate)	90
$F + BH \rightarrow FH + B$	1000–4000	$1.9 \times 10^{11} T^{0.67} \exp[-2.9 \times 10^3/RT]$	(Estimate)	192
$F + BH \rightarrow FH + B$	1000–4000	$2.3 \times 10^{11} T^{0.69} \exp[-4.2 \times 10^3/RT]$	(Estimate)	89
$F + BeH \rightarrow FH + Be$	298–2500	$1.3 \times 10^{11} T^{0.67} \exp[-2.5 \times 10^3/RT]$	(Estimate)	90
$F + BeH \rightarrow FH + Be$	1000–4000	$1.5 \times 10^{11} T^{0.67} \exp[-3.6 \times 10^3/RT]$	(Estimate)	192
$F + BeH \rightarrow FH + Be$	1000–4000	$2.5 \times 10^{11} T^{0.69} \exp[-2.4 \times 10^3/RT]$	(Estimate)	89
$F + KH \rightarrow FH + K$	298–2500	$4.3 \times 10^{10} T^{0.67} \exp[-9.9 \times 10^3/RT]$	(Estimate)	90
$F + LiH \rightarrow FH + Li$	298–2500	$9.1 \times 10^{10} T^{0.72} \exp[-8.5 \times 10^3/RT]$	(Estimate)	90
$F + LiH \rightarrow FH + Li$	1000–4000	$2.4 \times 10^{11} T^{0.69} \exp[-8.4 \times 10^3/RT]$	(Estimate)	89
$F + MgH \rightarrow FH + Mg$	298–2500	$5.2 \times 10^{11} T^{0.5} \exp[-0.6 \times 10^3/RT]$	(Estimate)	90
$F + NaH \rightarrow FH + Na$	298–2500	$6.7 \times 10^{10} T^{0.73} \exp[-8.0 \times 10^3/RT]$	(Estimate)	90
$F + NaH \rightarrow FH + Na$	1000–4000	$1.7 \times 10^{11} T^{0.69} \exp[-8.1 \times 10^3/RT]$	(Estimate)	89
$F + PH \rightarrow FH + P$	298–2500	$1.7 \times 10^{11} T^{0.69} \exp[-1.9 \times 10^3/RT]$	(Estimate)	90
$F + SH \rightarrow FH + S$	298–2500	$5.7 \times 10^{11} T^{0.5} \exp[-0.6 \times 10^3/RT]$	(Estimate)	90
$F + SiH \rightarrow FH + Si$	298–2500	$3.0 \times 10^{11} T^{0.5} \exp[-1.9 \times 10^3/RT]$	(Estimate)	90
$F + BeH_2 \rightarrow FH + BeH$	1000–4000	$2.3 \times 10^{10} T^{0.67} \exp[-2.1 \times 10^3/RT]$	(Estimate)	192
$F + BO_2 \rightarrow BOF + O$		$1.05 \times 10^{11} T^{0.5} \exp[-3.817 \times 10^3/T]$	(Estimate)	60
$F + B + M \rightarrow BF + M$		$3 \times 10^{16} T^{-0.5}$[a]	(Estimate)	60
$F + BF + M \rightarrow BF_2 + M$		$1 \times 10^{15} T^{-0.5}$[a]	(Estimate)	60
$F + BF_2 + M \rightarrow BF_3 + M$		$1 \times 10^{15} T^{-0.5}$[a]	(Estimate)	60
$F + BO + M \rightarrow BOF + M$		$1 \times 10^{15} T^{-0.5}$[a]	(Estimate)	60
$F + Xe + Ar \rightarrow XeF + Ar$	298	8.34×10^{14}[a]	Microwave discharge F_2	103
$F + Kr + Ar \rightarrow KrF + Ar$	298	$< 7.25 \times 10^{13}$[a]	Microwave discharge F_2	103
$F + XeF_2 \rightarrow$ products	298	$< 4.2 \times 10^8$	Microwave discharge F_2	103
$F + XeF_4 \rightarrow$ products	298	$< 4.2 \times 10^8$	Microwave discharge F_2	103

[a] Units = $cm^6\ mol^{-2}\ s^{-1}$.

5. *Iodine-Containing Halocarbons*

Tal'roze and co-workers reacted F atoms with CF_3I, studying the reaction by a mass spectral probe at the reaction cloud[187] and by mass spectral identification of the paramagnetic component of a molecular beam.[188] The rate constant, $(1.02 \pm 0.36) \times 10^{14}$ $cm^3\ mol^{-1}\ s^{-1}$, was calculated for the reaction, and the mechanism was postulated to be at least 95% abstraction:

$$F + CF_3I \rightarrow FI + CF_3 \qquad (234)$$

The exchange reaction 235, even though more favorable energetically,

$$F + CF_3I \rightarrow CF_4 + I \qquad (235)$$

occurs rarely, if at all, owing to the geometry of the molecule. The "turning out" of the molecule tetrahedron is difficult.[188] Bozzelli and Kaufman[182,183] arrived at a rate constant $k_{234} = (7.2 \pm 3) \times 10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$, compatible with that of Tal'roze and co-workers. The abstraction process (reaction 234) was deemed to be the correct process since CF_3 radicals were observed mass spectrometrically, while no atomic iodine was observed.

Tal'roze and co-workers[187] obtained a rate constant of $(1.2 \pm 0.42) \times 10^{14}$ cm^3 mol^{-1} s^{-1} for the reaction $F + CH_3I$. Because of the product rearrangement it was impossible to decide whether H or I abstraction or both H and I abstraction reactions occurred.

$$F + CH_3I \rightarrow HF + CH_2I \qquad (236)$$

$$F + CH_3I \rightarrow FI + CH_3 \qquad (237)$$

The exchange reaction 238 was ruled out since no CH_3F was observed.

$$F + CH_3I \rightarrow CH_3F + I \qquad (238)$$

A complete summary of the values obtained for the absolute rate constants for the reaction of fluorine atoms with halogen-substituted hydrocarbons is given in Table XIX. Relative rate constants for these reactions are presented in Table XX.

XII. Reaction with Miscellaneous Compounds

This section presents the few reported F atom reactions (most of them theoretical) which do not fall into any other category. Rosner and Allendorf[26,189] have reported on the reaction of F atoms with a number of solids. The rates were determined as an arbitrary figure referred to as "substrate atom removal probability". The following rate ratios were determined, B:C:Ti:Mo:W = 1:0.3:1:0.4:0.2. The molybdenum and tungsten reactions were found to be first order. Nordine et al.[29] reported a method that allowed rates of F atom–solid reactions to be measured by means of recording transient electrical resistance of a filament with time. They found the rate of the F atom reaction with platinum reached a maximum well below the melting point of platinum. Turner and Pimentel[190,191] reported that the reaction of F atoms with the rare gases Kr and Xe in matrices lead to the formation of KrF_2 and XeF_2, respectively.

Recently, Appelman and Clyne[103] reported a rate constant of 8.34×10^{14} cm^6 mol^{-2} s^{-1} for the termolecular reaction

$$F + Xe + Ar \rightarrow XeF + Ar \qquad (239)$$

The final product of the reaction was reported to be XeF_2 formed as in

$$2XeF \rightarrow Xe + XeF_2 \qquad (240)$$

The analogous Kr reaction was too slow to measure, but they estimated the upper limit for the rate constant as 7.25×10^{13} cm^6 mol^{-2} s^{-1}. Bimolecular reactions between F and XeF_2 and F and XeF_4 were also too slow to measure, having rate constants less than 4.2×10^8 cm^3 mol^{-1} s^{-1}.

Rate constants for hydrogen atom abstraction reactions by F atoms on a series of monohydrides have been estimated by a number of authors[89,90,192] and are reported in Table XXI. A number of theoretical rate constants for the reaction of F atoms with various boron-containing compounds[60] of importance in liquid propellant rocket engines also appear in Table XXI.

XIII. Concluding Remarks

We have attempted to present in this review a comprehensive summary of all work up to April 1975 in which kinetic measurements have been made on reactions of fluoride atoms. It is obvious from a survey of the references that the bulk of measurements in this area have been made over the last five years. The recent application of techniques of mass spectrometry, molecular beam analysis and laser studies have greatly assisted in these measurements and will continue to do so.

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XIV. Addendum

Since submitting this paper, several items of interest have come to our attention. Of prime importance are two review articles which have recently appeared. Foon and Kaufman[193] have published a review entitled, "Kinetics of Gaseous Fluorine Reactions", while Roland, Cramer, and Iyer[194] have reviewed the chemical reactions of fluorine atoms as studied by fluorine-18 tracer methods.

Several papers presenting results on reactions covered in this review have also been noted.

Grant and Root[195] studied the intermolecular isotope effect for the $F + H_2/D_2$ reactions by a nuclear recoil technique and found the ratio $k_{H_2}/k_{D_2} = (1.04 \pm 0.06) \exp(382 \pm 35)/RT$. Using the same technique Root and co-workers[196] obtained the rates of various hydrogen abstraction reactions relative to the addition reaction $^{18}F + C_3H_6 \rightarrow C_3H_6{}^{18}F$. The rates obtained relative to the addition reaction are as follows: CF_3H (26.6 ± 6.0), CF_3CH_3 (7.3 ± 2.3), CF_2H_2 (2.48 ± 0.11), D_2 (1.36 ± 0.03), H_2 (0.702 ± 0.004), CH_3F (0.47 ± 0.01), CD_4 (0.424 ± 0.003), CH_4 (0.272 ± 0.006), C_2H_6 (0.095 ± 0.005), c-C_3H_6 (0.085 ± 0.002), *neo*-C_5D_{12} (0.074 ± 0.002), c-C_6H_{12} (0.064 ± 0.005), *neo*-C_5H_{12} (0.050 ± 0.002), c-C_5H_{10} (0.030 ± 0.004).

Bemand and Clyne,[197] using the atomic resonance method to measure the fluorine atom concentration, found the rate constant for the reaction with Br_2 to be $(1.3 \pm 0.7) \times 10^{14}$ cm^3 mol^{-1} s^{-1} at 300 K.

McDowell et al.[198] found that the reaction of F atoms with SO_2 produced FSO_2. In this study the atoms were produced by photolysis of CF_3OF and the products were studied by EPR.

Goldberg et al.[199] found a two-step mechanism for the reaction of fluorine atoms with PF_3. At 300 K the rate constant for the first step $F + PF_3 \rightarrow PF_4$ was found to be $(8.6 \pm 0.6) \times 10^{12}$ cm^3 mol^{-1} s^{-1}, while that for the second $F + PF_4 \rightarrow PF_5$ was $(1.2 \pm 0.2) \times 10^{13}$ cm^3 mol^{-1} s^{-1}.

The thermochemistry involved in the combustion generation of F atoms was described by Axworthy et al.[200] in a paper presented to the Combustion Institute in 1974.

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