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A SURVEY OF KINETIC DATA OF COMPOUNDS CONTAINING FLUORINE

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Dana A. Brewer*

SUMMARY

Chlorofluoromethanes may have a significant effect on the level of ozone in the atmosphere. However, the role of fluorine-containing compounds has not been examined fully.

A tabulation of a search of the chemical kinetic literature published between 1953 and July 1975, is presented. The data are then evaluated with respect to acceptability and importance to the overall reaction balance in the atmosphere. Possible future research to elucidate important reaction processes is discussed.

INTRODUCTION

Recent awareness of the widespread uses of chlorofluoromethanes as aerosol propellants and refrigerants, the ubiquitous presence of chloromethanes, and the introduction of hydrogen chloride as a space shuttle solid-rocket exhaust component, have focused attention on possible reactions

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involving chlorine-containing compounds in the troposphere and stratosphere. Many of the halocarbons have been hypothesized to exert a significant impact on the environment in the near future by depleting ozone in the stratosphere through known homogeneous catalytic cycles, and by producing climate modifications through thermal-balance changes. Yet, current chemical kinetic and transport model predictions of these effects focus on the roles of chlorine and tend to dismiss as unimportant the possible roles of fluorine.

A complete tabulation of existing kinetic rate data for fluorine has not appeared in the open literature, partly because of the classification of rate data obtained from work on fluorine-containing liquid rocket propellants. Also, difficulties encountered in handling HF, F, and F_2 in the laboratory have significantly limited experimental investigations.

Prior to August 1975, a primary UV photolysis mechanism was the only accepted reaction process by which chlorofluoromethanes could be destroyed at significant rates in the stratosphere.

$$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$$

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

Attention was primarily focused on the formation of the chlorine atom since an odd oxygen destruction cycle directly follows.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

However, subsequent reactions of the substituted methyl radicals have neither been included in current kinetic models nor considered in adequate detail. Also, alternate reactions of halides with certain organic compounds, known or suspected to be present in the atmosphere, have not been sufficiently examined. This, in part, is attributed to the lack of absolute rate data since organic reactions characteristically produce wide product distributions and have complex mechanisms.

Further, the destruction of chlorofluoromethanes to form methylene intermediates directly had been overlooked before August 1975,

$$CFCl_3 + h\nu \rightarrow CFCl + 2Cl$$

$$CF_2Cl_2 + h\nu \rightarrow CF_2 + 2Cl$$

when preliminary work by the National Bureau of Standards was presented at the National Meeting of the Americal Chemical Society in Chicago. The consequences of this and/or other probable methylene formation mechanisms would seem to warrant at least as much attention as the methyl radical formation mechanism, since laboratory studies have shown that methylenes, once formed, react very rapidly with a variety of molecules. The author hypothesizes that methylene reactions may constitute important pathways by which chlorofluoromethanes undergo final degradation in the stratosphere.

This report presents the results of an extensive search of the chemical literature published between 1953 and July 1975, and includes a comprehensive tabulation and analysis of experimentally measured homogeneous gas-phase kinetic data for fluorine and simple hydrocarbon compounds. The report includes reactions from references 1 through 159, indicates which rate data appear acceptable and which rate data should be obtained, and proposes research that appears needed to elucidate important processes that may occur in the stratosphere.

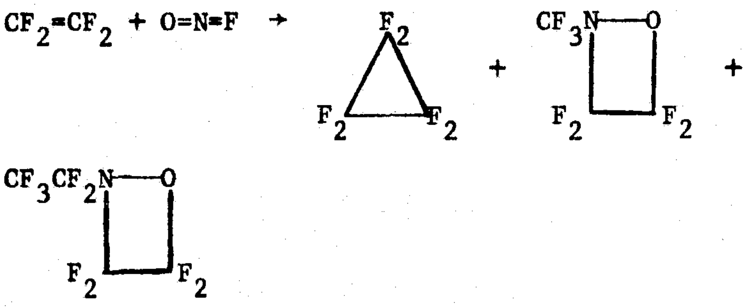
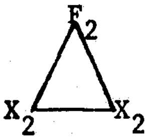
The tabulation of reactions is grouped into sections based on primary reactants. Some of the reactions listed are not balanced because the references did not specify a complete product list or a consistent mechanism. A key is provided to aid the reader in determining which reactions are elementary reactions(E), balanced overall reactions(O), or unbalanced overall reactions(ONB). The reactions are grouped as follows:

Key	Reaction
	Chlorine and Fluorine Reactants
E	1. $F + F + M \rightarrow F_2 + M$ $M = Ar, F_2, HF, F, H_2O, H_2, O_2, H, O, OH$
O	2. $F_2 + Cl_2 + M \rightarrow 2ClF + M$
E	3. $F + Cl_2 \rightarrow Cl + ClF$

Key	Reaction
E	4. $F_2 + Cl \rightarrow ClF + F$
E	5. $F + HCl \rightarrow ClF + H$
E	6. $F + ClF \rightarrow ClF_2$
O	7. $ClF_3 + Cl_2 \rightarrow 3ClF$
O	8. $F_2 + ClF \rightarrow ClF_3$
O	9. $F_2 + ClF_3 + M \rightarrow ClF_5 + M$
ONB	10. $O_2 + ClF + M \rightarrow O_3$ M = Ar
ONB	11. $Cl_2 + F_2 + O_2 \rightarrow ClF_3O$
O	12. $2ClF_3 + O_2 \rightarrow 2ClF_3O$
E	13. $F_2 + ClO_2 \rightarrow FClO_2 + F$
ONB	14. $F_2 + Cl_2 \rightarrow ClF + ClF_3 + ClF_2$
E	15. $F_2 + IF_5 \rightarrow IF_7$
E	16. $F + PH_3 \rightarrow HF + PH_2$
	Hydrogen, Fluorine, Oxygen Reactants
E	17. $H + F_2 \rightarrow HF + F$
E	18. $F + H_2 \rightarrow HF + H$
E	19. $H + F + M \rightarrow HF + M$ M = Ar, F_2, HF, F, H_2O, H_2, O_2, H, OH, O
E	20. $H + O + M \rightarrow OH + M$ M = F_2, HF, F
E	21. $H + OH + M \rightarrow H_2O + M$ M = F_2, HF, F
E	22. $O + O + M \rightarrow O_2 + M$ M = F_2, HF, F
E	23. $H + H + M \rightarrow H_2 + M$ M = F_2, HF, F
	Fluorine, Nitrogen, Oxygen, Hydrogen Reactants
O	24. $F_2 + 2NO + M \rightarrow 2FNO + M$

Key	**Reaction**
ONB	25. $F_2 + FNO_3 \rightarrow F_2 + FNO_2 + O_2$
O	26. $F_2O + NOF \rightarrow NO_2F + F_2$
O	27. $2FNO_3 \rightarrow 2FNO_2 + O_2$
O	28. $F_2 + 2NO_2 \rightarrow 2FNO_2$
O	29. $F_2 + N_2O \rightarrow OF_2 + N_2$
E	30. $NF_2 + F + M \rightarrow NF_3 + M$
E	31. $O_2(a^1\Delta) + NF(a^1\Delta) \rightarrow O_2(X^3\Sigma^-) + NF(b^1\Sigma^+)$
O	32. $NF_2(^2B_1) + H \rightarrow HF(v-2) + NF(b^1\Sigma^+)$
E	33. $F + NH_3 \rightarrow HF + NH_2$
E	34. $FO + FO \rightarrow 2F + O_2$
E	35. $F + O_3 \rightarrow OF + O_2$
O	36. $F_2O + 2F_2SO \rightarrow F_4SO + F_2SO_2$
O	37. $F_2 + F_2SO \rightarrow F_4SO$
	Carbon, Hydrogen, Oxygen Reactants
O	38. $CO + O + M \rightarrow CO_2 + M$
E	39. $CO + OH \rightarrow CO_2 + H$
ONB	40. $F + CO_2 + M \rightarrow CF_3OF + \frac{1}{2} O_2 + M$
ONB	41. $F_2 + CO + O_2 \rightarrow COF_2 + CO + (FCO)_2O_2$
O	42. $5CH_2O + 6O \rightarrow 3H_2 + 3CO + 2H_2O + 2CO_2 + O_2$
O	43. $CH_2O + OH \rightarrow CHO + H_2O$
ONB	44. $CF_2O + F_2 \rightarrow CF_3OF + CF_3OOCF_3$
O	45. $2CH_3O_2 \rightarrow 2CH_3O + O_2$
E	46. $CH_3O + O_2 \rightarrow CH_2O + HO_2$
E	47. $CH_3O + NO \rightarrow CH_2O + HNO$
E	48. $CH_3O + NO_2 \rightarrow CH_3ONO_2$
O	49. $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$

Key	Reaction
E	50. $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$
E	51. $CH_4 + OH \rightarrow CH_3 + H_2O$
E	52. $O + CH_4 \rightarrow OH + CH_3$
	Miscellaneous Reactants
E	53. $CH_3 + H_2S \rightarrow CH_4 + SH$
E	54. $CF_3 + H_2S \rightarrow CHF_3 + SH$
O	55. $3CH_4 + 6CF_3 \rightarrow C_2F_6 + CF_3CH_3 + 3CHF_3 + C_2H_6$
E	56. $CF + F + M \rightarrow CF_2 + M$
	Carbon-Carbon Double Bond Reactant
ONB	57. $O + CH_2{=}CH_2 \rightarrow CH_2O + CH_4 + CH_3CHO + CO + H_2 + O_2$
ONB	58. $4\ O + 4CF_2{=}CF_2 \rightarrow 3CF_2O + C_2F_4O^* + 2\,{}^1CF_2 + CF_2O_2$
ONB	59. $O(^3P) + CF_2{=}CFCl \rightarrow CF_2O + CFClO + CF_2 + CFCl$
ONB	60. $O(^3P) + CF_2{=}CCl_2 \rightarrow CF_2O + CCl_2O + CF_2 + CCl_2$
ONB	61. $F_2 + O_2 + CCl_2{=}CCl_2 \rightarrow CCl_2FCOCl + CCl_3COCl + CCl_2O$
O	62. $3CH_2{=}CH_2 + 5CCl_3Br \rightarrow CCl_3CH_2CH_2Br + 2CCl_3CCl_3 + 2CH_2BrCH_2Br$
O	63. $3CHF{=}CH_2 + 5CCl_3Br \rightarrow CCl_3CHFCH_2Br + 2CHFBrCH_2Br + 2CCl_3CCl_3$
O	64. $3CH_2{=}CHF + 5CCl_3Br \rightarrow CCl_3CH_2CHFBr + 2CHFBrCH_2Br + 2CCl_3CCl_3$
O	65. $3CH_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CH_2CF_2Br + 2CH_2BrCF_2Br + 2CCl_3CCl_3$
O	66. $3CH_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CH_2Br + 2CH_2BrCF_2Br + 2CCl_3CCl_3$
O	67. $3CHF{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CHFCF_2Br + 2CHFBrCF_2Br + 2CCl_3CCl_3$

Key	**Reaction**
O	68. $3CHF{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CHFBr + 2CHFBrCF_2Br + 2CCl_3CCl_3$
O	69. $3CF_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CF_2Br + 2CF_2BrCF_2Br + 2CCl_3CCl_3$
ONB	70. $CF_2{=}CF_2 + O{=}N{=}F \rightarrow$ 
	Carbon-Carbon Single Bond Reactant
O	71. $\frac{7}{2}F_2 + \frac{5}{2}Cl_2 + 6CCl_2{=}CCl_2 \rightarrow C_2Cl_6 + 2CCl_2FCCl_2F + 3CCl_2FCCl_3$
O	72.  $\rightarrow CF_2 + CX_2{=}CX_2$ X = Cl, Br, I
O	73. $C_3H_8 + M \rightarrow CH_3 + C_2H_5 + M$
O	74. $3C_2H_5Br \rightarrow C_2H_4 + 3HBr + C_2H_5 + C_2H_3$
E	75. $C_2H_6 + F \rightarrow HF + C_2H_5$
E	76. $C_2H_6 + Br \rightarrow C_2H_5 + HBr$
E	77. $C_2H_5F + Br \rightarrow CH_3CHF + HBr$
E	78. $CH_3CHF_2 + Br \rightarrow CH_3CF_2 + HBr$
E	79. $CH_3CF_3 + Br \rightarrow CH_2CF_3 + HBr$
E	80. $CHF_2CHF_2 + Br \rightarrow CHF_2CF_2 + HBr$
E	81. $CF_3CH_2F + Br \rightarrow CF_3CHF + HBr$
E	82. $CF_3CHF_2 + Br \rightarrow CF_3CF_2 + HBr$

Key	Reaction
O	83. $2CClF_2CClF_2 + F_2 \rightarrow 2CClF_2CF_3 + 2ClF$
O	84. $CF_3CClF_2 + F_2 \rightarrow C_2F_6 + ClF$
O	85. $4CCl_3CHCl_2 + Cl_2 + 2O_2 \rightarrow C_2Cl_6 + 2CCl_3COCl + 2COCl_2 + 4HCl$
O	86. $CCl_3CHCl_2 + F_2 \rightarrow HF + CCl_3CCl_2F$
	Methane and Substituted Methane Reactants
E	87. $F + CHF_3 \rightarrow HF + CF_3$
O	88. $F_2 + CHF_3 \rightarrow CF_4 + HF$
E	89. $Br + CHF_3 \rightarrow HBr + CF_3$
E	90. $F + CHClF_2 \rightarrow HF + CClF_2$
E	91. $F + CHCl_3 \rightarrow HF + CCl_3$
E	92. $F + CHCl_2F \rightarrow HF + CCl_2F$
E	93. $F + CH_2F_2 \rightarrow HF + CHF_2$
E	94. $Br + CH_2F_2 \rightarrow HBr + CHF_2$
E	95. $F + CH_2Cl_2 \rightarrow HF + CHCl_2$
E	96. $F + CH_3F \rightarrow HF + CH_2F$
E	97. $Br + CH_3F \rightarrow HBr + CH_2F$
E	98. $F + CH_3Cl \rightarrow HF + CH_2Cl$
O	99. $6F_2 + 5CH_3I \rightarrow 2CH_2F_2 + 2CH_3F + I_2 + 3HF + CH_2IF + IF^* + IF$
E	100. $F + CH_4 \rightarrow HF + CH_3$
E	101. $Br + CH_4 \rightarrow CH_3 + HBr$
O	102. $3CCl_4 + 6H + 2H_2 \rightarrow 6HCl + CH_2Cl_2 + CHCl_3 + CHCl$
E	103. $F + CCl_4 \rightarrow CCl_3 + ClF$
O	104. $F_2 + CCl_4 \rightarrow CCl_3F + ClF$

Key	**Reaction**	
O	105. $F_2 + CFCl_3 \rightarrow CF_2Cl_2 + ClF$	
O	106. $F_2 + CF_2Cl_2 \rightarrow CF_3Cl + ClF$	
O	107. $CF_3Cl + F_2 \rightarrow CF_4 + ClF$	
E	108. $CF_4 + M \rightarrow CF_3 + F + M$	
O	109. $CF_3Br + F \rightarrow CF_4 + Br$	
E	110. $CF_3Br + F \rightarrow BrF + CF_3$	
O	111. $F + CCl_3Br \rightarrow CFCl_3 + Br$	
O	112. $F + CCl_3Br \rightarrow BrF + CCl_3$	
O	113. $F + CF_3I \rightarrow CF_4 + I$	
O	114. $F + CF_3I \rightarrow IF + CF_3$	
	Methyl Radical Reactant	
E	115. $CF_3 + M \rightarrow CF_2 + F + M$	$M = Ar$
E	116. $CF_3 + CF_3 + M \rightarrow C_2F_6 + M$	$M = Ar$
E	117. $CH_3 + CH_3 \rightarrow C_2H_6$	
E	118. $CF_3 + F + M \rightarrow CF_4 + M$	
O	119. $CHFCl_2 + O_2 \rightarrow CO_2 + HF + 2Cl$	
E	120. $CH_3 + NO \rightarrow CH_3NO$	
E	121. $CH_3 + NO_2 \rightarrow CH_3NO_2$	
E	122. $CH_3 + CH_3NO \rightarrow (CH_3)_2NO$	
O	123. $2CHF_2Cl \rightarrow 2HCl + C_2F_4$	
E	124. $CF_3 + CF_3 \rightarrow C_2F_6$	
E	125. $CH_3 + CH_3F \rightarrow CH_4 + CH_2F$	
E	126. $CH_3 + CH_3Br \rightarrow CH_3Br + CH_3$	
E	127. $CH_3 + CH_3I \rightarrow CH_3I + CH_3$	

Key	Reaction
E	128. $CH_3 + CH_2F_2 \rightarrow CH_4 + CHF_2$
E	129. $CH_3 + CH_2ClBr \rightarrow CH_3 + CH_2Cl$
E	130. $CH_3 + CH_2ClI \rightarrow CH_3I + CH_2Cl$
E	131. $CH_3 + CF_2Br_2 \rightarrow CH_3Br + CF_2Br$
E	132. $CH_3 + CHF_3 \rightarrow CH_4 + CF_3$
O	133. $3CHCl_3 \rightarrow CCl_4 + 3HCl + CCl_2{=}CCl_2$
E	134. $CH_3 + CHCl_2Br \rightarrow CH_3Br + CHCl_2$
E	135. $CH_3 + CBr_4 \rightarrow CH_3Br + CBr_3$
E	136. $CH_3 + CCl_4 \rightarrow CH_3Cl + CCl_3$
E	137. $CH_3 + CCl_3Br \rightarrow CH_3Br + CCl_3$
E	138. $CH_3 + CF_3I \rightarrow CH_3I + CF_3$
E	139. $CF_3 + CH_3Br \rightarrow CF_3Br + CH_3$
E	140. $CH_3 + C_2H_5I \rightarrow CH_3I + C_2H_5$
	Methylene Reactant/Product
O	141. $CH_2CO \rightarrow CH_2 + CO$
O	142. $CH_2N_2 \rightarrow {}^1CH_2 + N_2$
E	143. $CF_2 + M \rightarrow CF + F + M$
O	144. $5CH_4 \rightarrow {}^3CH_2 + 2CH_3 + 3H_2 + C_2H_6$
E	145. $CF_2 + CFCl \rightarrow CF_2CFCl$
E	146. $2CF_2 \rightarrow C_2F_4$
O	147. $3H + 7CH_2N_2 + H_2 \rightarrow C_2H_4 + 2CH_4 + CHN_2 + C_2H_6 + 6N_2$
E	148. $CF_2 + F + M \rightarrow CF_3 + M$
O	149. $5CH_2CO + 4H_2 \rightarrow C_2H_6 + 5CO + C_2H_4 + CH_4 + 4H$
E	150. ${}^1CH_2 + CH_4 \rightarrow C_2H_6$

Key	**Reaction**
E	151. $^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2$
O	152. $^1CH_2 + H_2 \rightarrow CH_3 + H$
E	153. $^1CH_2 + H_2 \rightarrow {}^3CH_2 + H_2$
E	154. $^1CH_2 + M \rightarrow {}^3CH_2 + M$
E	155. $^3CH_2 + H_2 \rightarrow CH_3 + H$
E	156. $^3CH_2 + CH_4 \rightarrow 2CH_3$
O	157. $4CH_2N_2 + 2CH_4 \rightarrow C_2H_4 + 2C_2H_6 + 4N_2$
O	158. $CH_2N_2 + CO_2 \rightarrow H_2CO + CO + N_2$
O	159. $9CH_2CO + 9CH_3Cl \rightarrow 9CO + 2C_2H_4 + 2HCl + 2C_2H_6 + CH_4 + CH_2Cl_2 + 2C_2H_5Cl + C_2H_4Cl_2 + C_2H_3Cl$
E	160. $^1CH_2 + CH_2F_2 \xrightarrow{\text{abstraction}} C_2H_3F + HF$ $\xrightarrow{\text{insertion}} C_2H_4F_2$
E	161. $CF_2 + C_2F_4 \rightarrow \text{cyclo-}C_3F_6$
ONB	162. $^1CH_2 + CH_2Cl_2 \rightarrow CH_2ClCH_2Cl + CH_3CH_2Cl + C_2H_6$
O	163. $^1CH_2 + C_2H_6 \rightarrow C_3H_8$
ONB	164. $CH_2 + 3SO_2 \rightarrow CS_2 + H_2O + S + CO + CO_2$
E	165. $CF_2 + NO \rightarrow CF_2NO$
O	166. $CH_2CO + CH_3CH_2Cl \rightarrow \text{products}$

SYMBOLS

A	frequency factor in rate constant; has same units as rate constant
D	dissociation energy of a specific bond

e^-	electron
E_a	activation energy of the reaction; units are cal/mole unless otherwise noted
EPR	electron paramagnetic resonance spectroscopy
ESR	electron spin resonance spectroscopy
ΔG	Gibb's free energy of reaction
GC	gas chromatography
GLPC	gas liquid phase chromatography
h	Plank's constant
ΔH	enthalpy of reaction
ΔH_f^o	enthalpy of formation at 298° K
I_o	incident intensity of light
IR	infrared spectroscopy
J	photon flux, photons/sec-cm^2
k	rate constant in units of centimeters, molecules, and seconds (cm, mol, s)
k_b	Boltzmann constant
M	inert gas; collisional deactivator in a reaction

MS	mass spectrometry
NMR	nuclear magnetic resonance spectroscopy
P	pressure in torr
R	universal gas constant (1.987 cal/mole-^{o}K)
r	rotational quantum number
rds	rate determining step in a mechanism
ΔS	entropy of reaction
T	temperature in degrees Kelvin
t	translational quantum number
ΔU	internal energy of reaction in kcal/mole
UV	ultraviolet spectroscopy
v	vibrational quantum number
VPC	vapor phase chromatography
λ	wavelength in Angstroms
γ	collisional efficiency
$\neq$	activated complex
[ ]	concentration in moles/liter

*   molecule in excited state

KINETIC THEORY OF REACTIONS

The kinetic theory which forms the foundation for rate constant expressions is briefly outlined below to aid the reader in interpreting the contents of table 1.

Thermal reactions are those reactions that proceed by applying heat in the absence of external UV-visible radiation effects. They are primarily ground state processes; that is, initially both the reactants and products are mainly in their ground electronic and usually lower vibrational-rotational levels.

The simplest type of thermal reaction is the elementary reaction which may be unimolecular, bimolecular, or termolecular. Unimolecular or first order elementary reactions occur when a molecule in an excited state breaks apart to form one or more different species or products. Bimolecular or second order elementary reactions consist of two molecules or reactants colliding in a single step to form one or more products. Third order or termolecular elementary reactions have three reactants colliding in a single step to form one or more products that are different from the reactants. The products may be different compounds or the same compounds as the reactants but in different quantum states.

A collection of elementary reactions comprises a mechanism. A mechanism is postulated, based on experimentally determined data; it may or may not actually describe the correct way in which the molecules react in elementary reactions. For a one step mechanism, the elementary reaction is equal to the total reaction, and the order and the molecularity of the reaction are equivalent. However, when more than one elementary reaction describes the total reaction, it is no longer proper to speak of molecularity; when it is possible to express the empirical rate law in the form

$$\text{rate} = k[A]^m[B]^n$$

the order of the reaction is the sum of exponents in the rate equation. The rate constant, k, has units that reflect the order of the reaction. A first order reaction rate constant has the units of s^{-1}, a second order reaction has the units of $cm^2/mol\text{-}s$, and the units of a third order reaction are $cm^6/mol^2\text{-}s$.

The rate constant appearing in the rate equation may be formulated in several ways. It is common practice to express observed or empirical rate constants in the Arrhenius form,

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

where A is the frequency factor and E_a is the activation energy. The activation energy is approximately equal to the energy difference between the reactants in an average quantum state and the transition state, the top of the average potential energy barrier along the reaction coordinate. When a complex mechanism is used to describe the reaction, the activation energy for the total reaction is some combination of the activation energies for the elementary reactions.

Transition state theory, applicable to bimolecular and termolecular reactions, is a theory generally used to predict rate constants rather than evaluate experimental data. The transition state or activated complex is defined as those configurations that occur at the top of a potential energy barrier along the reaction coordinate. The rate constant for a bimolecular reaction between two nonlinear polyatomic reactants A (comprised of n_a atoms) and B (comprised of n_b atoms) is

$$k = \left(\frac{k_b T}{h}\right) \frac{f_t^{\neq} f_r^{\neq} f_v^{\neq}}{f_{t,A} f_{r,A} f_{v,A} f_{t,B} f_{r,B} f_{v,B}} \exp\left(-\frac{E_o}{RT}\right)$$

where f_t, f_r, and f_v are the statistical mechanical partition functions for translation, rotation, and vibration, respectively, and E_o is the difference between the ground state energy levels of the initial and transition states. The partition functions, $f_{v,A}$ and $f_{v,B}$, are evaluated for 3n-6 vibrational degrees of freedom while $f_v^{\neq}$ is evaluated for 3n-7 degrees of freedom. The 3n-7 degrees of vibrational freedom in the transition state result because the theory treats one vibrational degree of freedom as a translation along the reaction coordinate.

The transition state may be described by thermodynamic quantities.[56] The free energy of activation, $\Delta G^{\neq}$, and the enthalpy of activation, $\Delta H^{\neq}$, may be used to write down the entropy of activation

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T}$$

The empirical activation energy is related to the enthalpy of activation by

$$\Delta H^{\neq} = E_a - nRT$$

where n is the molecularity of the reaction. When a detailed temperature dependence of the rate constant for a gas-phase reaction is known, such as

$$k = A\, T^m \exp\left(-\frac{E_o}{RT}\right)$$

E_o and E_a may be related by

$$E_a - E_o = mRT$$

and

$$\Delta H^{\neq} = E_o + (m-n)RT$$

The activation energies for the forward and reverse processes are also related to the enthalpy by

$$\Delta H = E_{a,f} - E_{a,r} .$$

Unimolecular reactions are treated by employing the Lindemann-Hinshelwood mechanism:

$$A + M \rightarrow A^* + M \qquad 1)$$
$$A^* + M \rightarrow A + M \qquad 2)$$
$$A^* \rightarrow B + C . \qquad 3)$$

Step 3 is a true unimolecular reaction. The rate of disappearance of A is expressed as

$$\frac{d[A]}{dt} = -k_1[A][M] + k_2[A^*][M]$$

the rate of intermediate formation as

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_2[A^*][M] - k_3[A^*]$$

and the rate of product formation as

$$\frac{d[B]}{dt} = \frac{d[C]}{dt} = k_3[A^*] \ .$$

When the steady state approximation, $\frac{d[A^*]}{dt} = 0$, is applied, then the equations reduce to

$$[A^*] = \frac{k_1[A][M]}{k_2[M] + k_3}$$

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{k_1k_3[A][M]}{k_2[M] + k_3} \ .$$

Taking the high pressure limit of M, or when M is in high concentration relative to A, B, and C, $k_2[M] >> k_3$, and the equations reduce to

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{k_1k_3[A]}{k_2} \ .$$

Conversely, when M is in low concentration, that is $k_3 >> k_2[M]$, then

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k_1[A][M] \ .$$

The rate constants obtained from the application of the Lindemann mechanism are qualitatively correct but quantitatively poor. Much more accurate treatments of unimolecular reactions have resulted from the treatment of the data with the Rice, Ramsberger, Kassel, and Marcus (RRKM) theory; this theory looks at individual rate constants as functions of the molecular energy.

Photochemical reactions are those reactions which proceed when light of a specific wavelength range is absorbed and a reactive state/specie is produced. The reactions generally occur at a much lower temperature than if light were absent, and, by definition, may involve radicals or molecules in excited states.

$$A + h\nu \rightarrow A^{*} \rightarrow \text{products}$$

Evaluation of rate constants for these reactions involves an application of Beer's law,

$$I_a = I_o\,(1 - \exp(-\,\beta N d))$$

where I_a is the absorbed intensity and I_o is the incident intensity of light, β is the molecular absorption coefficient, d is the thickness of the sample, and N is the number of molecules per cubic centimeter. The rate constant for an elementary photolytic reaction is expressed in terms of a quantum yield,

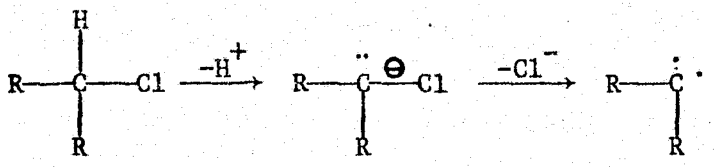
$$\Phi = \frac{\text{number of molecules formed}}{\text{number of quanta absorbed}}\ ,$$

while the overall rate constant is a function of both light intensity and the concentrations of reactants and products.

METHYLENE

Methylene, also called carbene, is a reactive intermediate in many chemical reactions. The simplest methylene, CH_2, is a diradical which may exist either as a triplet, $^3CH_2$, having two unpaired electrons, or as a singlet, $^1CH_2$, where the electrons are paired. Numerous theoretical calculations on CH_2 have shown that the triplet is the ground state, and there is an energy difference of only a few kilocalories between the ground state triplet and the first excited state singlet.[85]

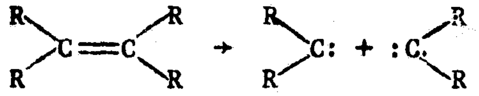
Carbenes are primarily formed in two ways,[101] by α-elimination and by disintegration of a double bond. In α-elimination, a carbon loses a group without its electron pair and then a group with its pair, usually a halide ion:



$$\mathrm{R{-}\overset{H}{\underset{R}{C}}{-}Cl} \xrightarrow{-H^{+}} \mathrm{R{-}\underset{R}{\ddot{C}}{}^{\ominus}{-}Cl} \xrightarrow{-Cl^{-}} \mathrm{R{-}\underset{R}{\overset{\cdot\cdot}{C}}\cdot}$$

R is any other substituent. In most cases of α-elimination, the positive group is lost first, followed by a negative group; however, it is possible for the negative group to be removed first or for both groups to be removed simultaneously.

Carbenes may also be formed when a double bond disintegrates; each doubly bonded atom retains an electron pair:



The two most important ways of generating carbenes, the photolysis of ketene and diazomethane, are formed in this way:

$$CH_2=C=O \xrightarrow{h\nu} :CH_2 + CO$$

$$CH_2=N=N \xrightarrow{h\nu} :CH_2 + N_2.$$

The reactions of carbenes are quite different from the reactions of other intermediates, cations, anions, and radicals. While recombination is an important reaction of radicals such as the methyl radical, it is a relatively unimportant reaction of carbenes. This is true because, when both radicals and carbenes are in the presence of stable molecules and reactive species, carbenes are more reactive; thus the mean lifetimes are much shorter, and the probability of recombination is reduced.

Important reactions of carbenes are abstraction, insertion, and addition to a double bond. Methylene can abstract a hydrogen atom to yield free radicals,

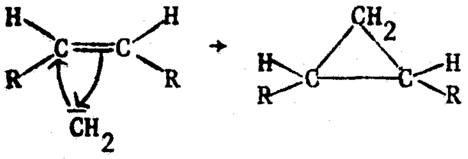
$$:CH_2 + CH_3CH_3 \rightarrow {}^{\cdot}CH_3 + CH_3CH_2{}^{\cdot} \quad .$$

The insertion reaction,

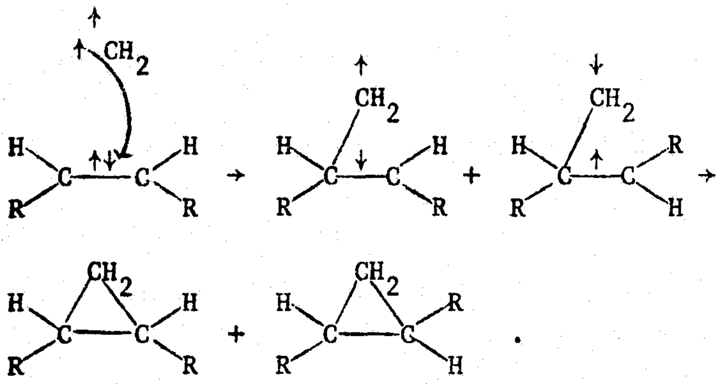
$$:CH_2 + CH_3CH_3 \rightarrow CH_3CH_2CH_3$$

occurs in competition with the abstraction reaction for the homogeneous gas phase reactions surveyed in table 1; workers have reported that abstraction predominates over insertion in all cases. Thus, the insertion reaction is more difficult to study, and more than one product is formed in methylene reactions.

The products formed when methylene adds to a double bond depend upon whether methylene is a triplet or a singlet. In the reaction of the singlet,



both electron pairs move simultaneously, resulting in retention of the configuration of the substituents around the original carbons forming the double bond. On the other hand, since the electrons in the triplet methylene are unpaired and cannot both form one covalent bond, the electrons do not move simultaneously, and the configuration about the double bond is not retained. For example,



The reactivities of methylenes decrease with increasing substitution in the order of $CH_2 > CHCl > CCl_2 > CHF > CF_2$. The ground state multiplicities also change when substituted carbenes are compared with unsubstituted methylene: the ground state of CH_2 is a triplet while the ground state of CF_2 is believed to be a singlet.[85]

REACTION RATE DATA

Table 1 is a compilation of experimentally determined rate data. The data are limited to the temperature and wavelength ranges that occur in the troposphere and stratosphere ($T \leq 400\ ^{o}K$, $\lambda \geq 1200$ Å). They do not include reactions with a carbon chain length greater than two or reactions that require unusual, liquid, or solid phase catalysts. Unless otherwise stated, all data follow Arrhenius kinetics; that is, the rate constant is expressed in the form

$$k = A \exp(-E_a/RT) .$$

Those references that include a wavelength are photolytic reactions; that is, they require either photolytic activation to produce the reactants or photolytic energy to overcome an energy barrier of an elementary reaction in the mechanism. All studies utilizing a shock tube are investigations of reactions occurring thermally. Further, an elementary reaction in a mechanism is photolytically induced only when light energy ($h\nu$) specifically appears in the step. No attempt was made to correct any obvious errors in the kinetic data reviewed in table 1. However, all rate data were transformed into consistent concentration units to aid in comparing rate data of several authors. All error limits noted are those stated in the references. When thermodynamic enthalpy is noted, a negative sign indicates exothermicity.

Table 1.- Kinetic Data

1. $F + F + M \rightarrow F_2 + M$

Ref.	Kinetic Methods	Rate Data	Comments
9 Bahn, et. al. (1969)	Recommended rate constants	rate = $k[F]^2[M]$	
		$k = \frac{1.60x10^{-32}}{T}$ cm^6/mol^2-s	M = Ar, T in °K
		$k = \frac{1.6x10^{-32}}{T}$ cm^6/mol^2-s	$M = F_2$
		$k = \frac{3.2x10^{-32}}{T}$ cm^6/mol^2-s	M = HF
		$k = \frac{6.4x10^{-32}}{T}$ cm^6/mol^2-s	M = F
		$k = \frac{6.4x10^{-32}}{T}$ cm^6/mol^2-s	$M = H_2O$
		$k = \frac{1.3x10^{-31}}{T}$ cm^6/mol^2-s	$M = H_2$
		$k = \frac{2.1x10^{-31}}{T}$ cm^6/mol^2-s	$M = O_2$
		$k = \frac{3.2x10^{-31}}{T}$ cm^6/mol^2-s	M = H
		$k = \frac{6.4x10^{-31}}{T}$ cm^6/mol^2-s	M = O
		$k = \frac{6.4x10^{-31}}{T}$ cm^6/mol^2-s	M = OH
57 Ganguli, et. al. (1974)	T = 295°K	$k_{295°K} = 8.02x10^{-35}$ cm^6/mol^2-s	M = Ar
	F atoms from microwave discharge	$-\frac{d[F]}{dt} = 2k[F]^2[M] + k_{wall}[F]$	Error in rate constant is ± factor of 2
	P = 10-81 torr		
	Teflon flow reactor		
	Chemiliminescent titration of F_2 with Cl_2 for product analysis		

Table 1.- Continued

1. $F + F + M \rightarrow F_2 + M$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
110 Modica, et. al. (1968)	Shock tube $T = 1700 - 3000^{\circ}K$ Product Detection: UV at 2660 Å	$A = 4.03x10^{-37} cm^6/mol^2\text{-}s$ E_a = 12115cal/mole	M = Ar
79 Johnson, et. al. (1964)	Reverse reaction studied Shock tube $T = 1300\text{-}1600^{\circ}K$ Product analysis: spectrophotometric	$A = (1.23 \pm 0.58)x10^{-11}$ $cm^3/mol\text{-}s$ E_a = 29.97±3.51 kcal/mole	M = Ar
79 Johnson, et. al. (1964) 131,132 Seery, et. al. (1966)	Reverse reaction studied Shock tube $T = 1300\text{-}1600^{\circ}K$ Product analysis: spectrophotometric	$A = (7.6 \pm 4.0)x10^{-12}$ $cm^3/mol\text{-}s$ E_a = 28.49±2.15 kcal/mole	M = Ar
39 Diesen (1966)	Reverse reaction studied Shock tube $T = 1650 - 2700^{\circ}K$ Product analysis: MS	$A = (2.3 \pm 2.2)x10^{-12}$ $cm^3/mol\text{-}s$ E_a = 23.66±1.24 kcal/mole	M = Ne
40 Diesen (1968)	Reverse reaction studied Shock tube $T = 1400\text{-}2000^{\circ}K$ Product analysis: MS	$A = (3.89 \pm 4.27)x10^{-11}$ $cm^3/mol\text{-}s$ E_a = 34.89±3.08 kcal/mole $A = (6.46 \pm 3.55)x10^{-12}$ $cm^3/mol\text{-}s$ E_a = 28.68±2.15 kcal/mole	M = Ne M = Ar
39 Diesen (1966) 40 Diesen (1968)	Reverse reaction studied Shock tube Product analysis: MS	$A = (2.01 \pm 2.57)x10^{-11}$ $cm^3/mol\text{-}s$ E_a = 33.08±1.70 kcal/mole	M = Ne

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
1.	$F + F + M \rightarrow F_2 + M$ (continued)		
132 Seery, et. al. (1966)	Reverse reaction studied	Efficiency ratio of third bodies: Ne : Ar = 1 : 1.5	
2.	$Cl_2 + F_2 + M \rightarrow 2ClF + M$		
50 Fletcher, et. al. (1969)	T = 353-401 °K Product detection: IR of ClF at λ = 12755 Å	$A = 1.84 x 10^{-2} cm^{3/2}/mol^{3/2}\text{-}s$ E_a = 19800 cal/mole rate $= k[F_2][Cl_2]^{1/2}$	Mechanism — ΔH (kcal/mole) 1) $F_2 + M \rightarrow 2F + M$ — 38 2) $F + Cl_2 \rightarrow ClF + Cl$ — -3 3) $Cl + F_2 \rightarrow ClF + F$ — -23 4) $Cl + F + M \rightarrow ClF + M$ — -61 5) $F + F + M \rightarrow F_2 + M$ — -38 6) $Cl + Cl + M \rightarrow Cl_2 + M$ — -58
3.	$Cl_2 + F \rightarrow Cl + ClF$		
16 Blauer, et. al. (1971)	T = 1700-2200°K Shock tube Reverse reaction studied Product detection: Optical densities	$E_{a,r}$ ≈ 12 kcal mole Rate constants determined for some elementary reactions: $ClF + M \rightarrow Cl + F + M$ $A = 1.7x10^{-14\pm3} cm^3/mol\text{-}s$ E_a = 61300±3000 cal/mole $Cl_2 + M \rightarrow Cl + Cl + M$ $A = (3.2\pm2.4)x10^{-11} cm^3/mol\text{-}s$ E_a = (46450±1500) cal/mole	Estimated from Evans-Polanyi rule Endothermic exchange reactions postulated as part of mechanism

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
3.	$Cl_2 + F \rightarrow Cl + ClF$(continued)		
31 Clyne, et. al. (1973)	$T = 300^oK$ F atoms from microwave discharge Fast flow reactor Product analysis: MS	$\Delta U^o_{298} = -2.5$ kcal/mole $k = (1.1 \pm 0.3) x 10^{-10}$ cm^3/mol-s	
57 Ganguli, et. al. (1974)	F atoms from microwave discharge Chemiluminescent titration of F_2 with Cl_2 Teflon flow reactor P = 10-81 torr	ΔH = 3 ± 2 kcal/mole	Error in rate data is ± factor of 2
152 Warnatz, et. al. (1971)	Flow reactor F atoms from microwave discharge Product analysis: MS	$A = 9.13 x 10^{-10}$ cm^3/mol-s $E_a = 1400$ cal/mole	
4.	$F_2 + Cl \rightarrow ClF + F$		
57 Ganguli, et. al. (1974)	P = 10-81 torr $T = 295^oK$ Chemiluminescent titration of F_2 with Cl_2 Teflon flow reactor	$\Delta H = -23 \pm 2$ kcal/mole $k < 1.7 x 10^{-15}$ cm^3/mol-s	Error in rate data is ± factor of 2
5.	$F + HCl \rightarrow ClF + H$		
91 Kompa, et al. (1972)	Flash photolysis	$k = 2.5 x 10^{-11}$ cm^3/mol-s	

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
5. $F + HCl \rightarrow ClF + H$ (continued)			
84 Jonathan, et. al. (1971)	Flow system	$k_{298^oK} = 3.2x10^{-12}$ cm^3/mol-s	
	Product analysis: IR Chemiluminescence	E_a = 2.54 kcal/mole	Assumed
	P = 80-100 torr	A = $2.2x10^{-10}$ cm^3/mol-s	Assumed
115 Pollack, et. al. (1973)	T = 298^oK	$k_{298^oK} = 1.2x10^{-11}$ cm^3/mol-s	
	Fast flow reactor		
	Product detection: GC, MS, IR		
88 Kirsch, et. al. (1972)	T = 1700^oK	E_a = 1 kcal/mole (approximate)	HF detection used to deduce rate of reaction 5
	HF detection: IR chemiluminescence	7.9% HCl in v=1 vibrational level	
	F from microwave discharge		
	Vibrational study of $F + HCl(v,r,t) \rightarrow$ $HF(v,r,t,) + Cl$ v = vibrational state r = rotational state t = translational state		
6. $ClF + F \rightarrow ClF_2$			
99 100 Mamantov, et al. (1970, 1971)	T $\leqq$ 25^oK Product analysis: IR F atoms from Hg lamp: λ = 2800-4200 Å		Decay at higher temperatures by 2 mechanisms: 1) $ClF_2 + F \rightarrow ClF_3$ 2) $2ClF_2 \rightarrow ClF + ClF_3$

Table 1.- Continued

7. $ClF_3 + Cl_2 \rightarrow ClF$

Ref.	Kinetic Methods	Rate Data	Comments
130 Schmitz, et. al. (1947)			Quantitative reaction
8. $F_2 + ClF \rightarrow ClF_3$			
126 San Roman, et. al. (1970)	$\lambda = 3650$ Å Photolytic reaction $T = 303 - 323\ ^{\circ}K$	With sufficient F_2, quantum yield of $ClF_3 = 1.0$ mol/photon	Quantum yield is independent of: (1) which reactant absorbs energy (2) added oxygen (3) total pressure (4) ClF_3 concentration (5) reactant concentration (6) temperature
9. $F_2 + ClF_3 + M \rightarrow ClF_5 + M$			
92 Kreiger, et. al. (1966)	$T = 289\text{-}343^{\circ}K$ $\lambda = 3650$ Å Product analysis: UV	At 298°K, quantum yield = 0.5 mol/photon $\frac{d[ClF_5]}{dt} = \frac{k\ J_{abs}}{\frac{k'[ClF_3]}{[M']} + 1 + \frac{k''}{[M]}}$ $k = \frac{k_3}{k_3+k_4}$ $k'' = \frac{k_7k_4}{k_3k_6+k_4k_6}$ $k' = \frac{k_4k_5}{k_3k_6+k_4k_6}$	O_2 inhibition Mean lifetime of $ClF_5^* = 10^{-9}s$ Mechanism: (1) $F_2 + h\nu \rightarrow 2F$ (2) $F + ClF_3 + M \rightarrow ClF_4 + M$ (3) $ClF_4 + F \rightarrow ClF_5^*$ (4) $ClF_4 + F \rightarrow ClF_3 + F_2$ (5) $ClF_5^* + ClF_3 \rightarrow 2ClF_4$ (6) $ClF_5^* + M \rightarrow ClF_5 + M$ (7) $ClF_5^* \rightarrow ClF_4 + F$

Table 1.- Continued

9. $F_2 + ClF_3 + M \rightarrow ClF_5 + M$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
92 (continued)		At 298°K, k=0.50, k'=2.00, k" = 80. Temperature efficiency = $-0.97 \pm 0.01/10^{\circ}$ rise $M' = \gamma_{F_2}P_{F_2} + \gamma_{ClF_5}P_{ClF_5} + \gamma_x P_x$; $x \neq ClF_3$ $\gamma_{F_2} : \gamma_{ClF_5} : \gamma_{N_2} : \gamma_{Ne}$ = 1 : 0.4 : 0.22 : 0.18	
10.	$O_2 + ClF + M \rightarrow O_3$		
100 Mamantov, et. al. (1971)	T = 15°K λ = 2800 - 4200 Å Product detection: IR		M = Ar Product identification only
11.	$Cl_2 + F_2 + O_2 \rightarrow ClF_3O$		
114 Pilipovich, et. al. (1972)	λ = 1700 - 2967 Å T = 213°K Product analysis: IR, UV, vapor pressure, gas density		Product identification Yield: 44.6% after 6 hours
12.	$2ClF_3 + O_2 \rightarrow 2ClF_3O$		
114 Pilipovich, et. al. (1972)	λ = 1700 - 2967 Å Product analysis: IR, UV, vapor pressure, gas density		Product identification Yields of ClF_3O: 0% at T = 288°K 79% at T = 213°K

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
12.	$2ClF_3 + O_2 \rightarrow 2ClF_3O$ (continued)		
			Mechanism: 1) $ClF_3 \rightleftarrows ClF + F_2$ 2) $O_2 \rightarrow 2\ O$ 3) $ClF + O \rightarrow ClOF$ 4) $ClOF + F_2 \rightarrow ClF_3O$
13.	$F_2 + ClO_2 \rightarrow FClO_2 + F$		
6 Aymonino, et. al. (1954)	T = 227 - 247 °K P = 50 - 500 torr	E_a = 8.5 ± 0.4 kcal/mole rate = $k[F_2][ClO_2]$ $k_{227\ ^oK} = 3.8 \times 10^{-22}$ cm^3/mol-s $k_{237\ ^oK} = 8.6 \times 10^{-22}$ cm^3/mol-s $k_{247\ ^oK} = 1.7 \times 10^{-21}$ cm^3/mol-s	
14.	$Cl_2 + F_2 \rightarrow ClF_3 + ClF + ClF_2$		
100 Mamantov, et. al. (1971)	T = 14 °K λ = 2800 - 4200 Å Product detection: IR		Stoichiometry dependence observed
124 Ruff, et. al. (1930)		ΔH = 3.3 kcal/mole in liquid phase	ClF_3 dimerizes in gas phase with non-ideal behavior
15.	$F_2 + IF_5 \rightarrow IF_7$		
49 Fischer, et. al. (1957)	T = 328.8 - 366.2 °K Vacuum line Product detection: pressure measurements	rate = $k[F_2][IF_5]$ E_a = 14 kcal/mole	Table of raw rate data

Table 1.- Continued

16.	$F + PH_3 \rightarrow HF + PH_2$		
Ref.	Kinetic Methods	Rate Data	Comments
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: GC, MS, IR	$k \geqq 2.2 \times 10^{-11}$ cm^3/mol-s	
17.	$H + F_2 \rightarrow HF + F$		
1 Albright, et. al. (1969)	T = 294 - 565°K Product analysis: molecular beam MS	$\Delta H = -98$ kcal/mole $A = (2.0 \pm 0.6) \times 10^{-10}$ cm^3/mol-s $E_a = 2400 \pm 200$ cal/mole	Photolytic activation
120 Rabideau, et. al. (1972)	T = 300°K Fast flow reactor Product detection: EPR X-band spectrometer	$k = (4.2 \pm 0.3) \times 10^{-12}$ cm^3/mol-s	
31 Clyne, et. al. (1973)	Fast flow reactor Product analysis: MS	$k = 2.5 \times 10^{-11}$ cm^3/mol-s $E_a \leqq 2$ kcal/mole Collisional efficiency ≅ 0.1	≦ 100 chain cycles
18.	$F + H_2 \rightarrow HF + H$		
31 Clyne, et. al. (1973)	T = 300°K F atoms from microwave discharge Fast flow reactor Product analysis: MS	$k_{H_2} = (2.5 \pm 1.25) \times 10^{-11}$ cm^3/mol-s	
75 Homann, et. al. (1970)	Product analysis: MS, gas titration Flow system	$A = 2.6 \times 10^{-10}$ cm^3/mol-s $E_a = 1600$ cal/mole	

Table 1.- Continued

18. $F + H_2 \rightarrow HF + H$(continued)

Ref.	Kinetic Methods	Rate Data	Comments
91 Kompa, et. al. (1972)	Flash photolysis	$k_{298^oK} = 6.3 \times 10^{-11}$ cm^3-mol-s	Deactivation probabilities (P): For $HF(v=1) + HF(v=0) \xrightarrow{v,t} 2HF(v=0)$ $P = 2 \times 10^{-2}$ For $HF(v=1) + H_2(v=0) \xrightarrow{v,v} HF(v=0)$ $P = 3 \times 10^{-5}$
120 Rabideau, et. al. (1972)	$T = 300^oK$ Fast flow reactor Product determination: EPR X-band spectrometer	$k = (6.6 \pm 1.7) \times 10^{-12}$ cm^3/mol-s	
41, 42 Dodonov, et. al. (1969, 1971)	$T = 300 - 400$ ^oK	$k = (3 \pm 1) \times 10^{-11}$ cm^3/mol-s	
52 Foon, et. al. (1971)	F atoms from microwave discharge Static system Product analysis: GC	k_{298} $^oK = 7.4 \times 10^{-13}$ cm^3/mol-s $A = 5.12 \times 10^{-13}$ cm^3/mol-s(assumed) $E_a = 5.20$ kcal/mole	
94 Levy, et. al. (1968)	$T = 395 - 435$ ^oK $P_{total} = 645$ torr $P_{O_2} = 85 - 500$ torr Product detection: UV, visible	Rate decreases with O_2 addition but reaches a limiting value at $P_{O_2} = 100$ torr Limiting rate law: $-\frac{d[F_2]}{dt} = k[F_2][H_2]^{1/2}$ Total $E_a = 16.7$ kcal/mole $H_f^o(FOO) = 3.5$ kcal/mole	Thermal activation Study of O_2 inhibition of rate Mechanism: 1) $H + F_2 \rightarrow HF + F$ E_a 5-7 kcal/mole 2) $F + O_2 + M \rightarrow F\text{-}O\text{-}O + M$ 3) $FOO + H_2 \rightarrow HF + O_2 + H$ Light has no effect on rate

Table 1.- Continued

18. $F + H_2 \rightarrow HF + H$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
25 Cadle, et. al. (1963)	Thermal reaction	Limiting rate = $k[F][H_2]^{1/2}$ $k_{overall} = 4.5 \pm 0.6 x 10^{-3} s^{-1}$	Mechanism for O_2 inhibition reaction from data of reference 94: 1) $F + H_2 \rightarrow HF + H$ 2) $H + O_2 + M \rightarrow HO_2 + M$ 3) $HO_2 + F_2 \rightarrow HF + O_2 + F$ 4) $HO_2 + F \rightarrow HF + O_2$ 5) $H + O_2 \rightarrow OH + O$ 6) $O + H_2 \rightarrow OH + H$ 7) $OH + H_2 \rightarrow H_2O + H$ Reaction 2 predominates below 500°K with large $[O_2]$
22 Brokaw (1965)	$T = 383^{o}K$		Mechanism (no O_2) from data of reference 94: $F + H_2 \rightarrow HF + H$ exothermic $H + F_2 \rightarrow \alpha HF^* + (1-\alpha)HF + F$ exothermic $HF^* + F_2 \rightarrow HF + 2F$ $HF^* + M \rightarrow HF + M$ $2F + M \rightarrow F_2 + M$ $M = N_2, H_2$

Table 1.- Continued

18.	$F + H_2 \rightarrow HF + H$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
95 Levy, et. al. (1968)	$T = 288.2 \pm 0.5\,^\circ K$ Mixtures of H_2, F_2, O_2, H_2 $\lambda = 3130$ Å $I_o = (1.11 \pm 0.07) \times 10^{17}$ quanta/s	$E_{a,3} = 1.5 \pm 0.3$ kcal/mole $-\frac{d[F_2]}{dt} = \frac{1}{2}\{k_2[F][H_2] + k_3[H][F_2] + k_5[F_2][HO_2] + k_6[F][HO_2]\}$ At P = 760 torr, T = 288°K, $\frac{k_3}{k_4} = 0.193 \pm 0.019$	Mechanism: 1) $F_2 + h\nu \rightarrow 2F$ 2) $F + H_2 \rightarrow HF + H$ 3) $H + F_2 \rightarrow HF + H$ 4) $H + O_2 + M \rightarrow HO_2 + M$ 5) $HO_2 + F_2 \rightarrow HF + O_2 + F$ 6) $F + HO_2 \rightarrow HF + O_2$
95 Levy, et. al. (1968)	$T = 395 - 435\,^\circ K$ Thermal reaction	Limiting rate for $[O_2] >> [F_2]$ $\text{rate}_{lim} = k[F_2][H_2]^{1/2}$ Step 1: $E_a = 37$ kcal/mole Step 5: $E_a = 5\text{-}6$ kcal/mole $k_3 = 2.95 \times 10^{-12}$ cm^3/mol-s $k_4 = 2.5 \times 10^{-32}$ cm^6/mol^2-s	O_2 inhibiton study Mechanism: $F_2 + M \xrightarrow{k_1} 2F + M$ Other steps same as photolytic reaction steps 2-6 (ref. 95)
48 Fettis, et. al. (1964)	$T = 195 - 351\,^\circ K$ F atoms from microwave discharge Product analysis: GC	Transition state theory used to treat rate date $A = 7.83 \times 10^{-11}$ cm^3/mol-s $E_a = 1710$ kcal/mole $\Delta S_t^{\neq} = 6.99$ cal/mole°K $\Delta S_r^{\neq} = 4.92$ cal/mole°K $\Delta S_v^{\neq} = 0.8$ cal/mole°K	

Table 1.- Continued

19.	$H + F + M \rightarrow HF + M$		
Ref.	**Kinetic Methods**	**Rate Data**	**Comments**
9 Bahn, et. al. (1969)	Recommended rate constants	rate = $k[H][F][M]$	T in °K
		$k = \frac{6.9x10^{-30}}{T}$ cm^6/mol^2-s	$M = Ar, F_2$
		$k = \frac{1.4x10^{-29}}{T}$ cm^6/mol^2-s	M = HF
		$k = \frac{2.7x10^{-29}}{T}$ cm^6/mol^2-s	$M = F, H_2O$
		$k = \frac{5.5x10^{-29}}{T}$ cm^6/mol^2-s	$M = H_2$
		$k = \frac{9.0x10^{-29}}{T}$ cm^6/mol^2-s	$M = O_2$
		$k = \frac{1.4x10^{-28}}{T}$ cm^6/mol^2-s	M = H
		$k = \frac{2.8x10^{-28}}{T}$ cm^6/mol^2-s	M = OH, O
20.	$H + O + M \rightarrow OH + M$		
9 Bahn, et. al. (1969)	Recommended rate constants	rate = $k[H][O][M]$	T in °K
		$k = \frac{1.1x10^{-29}}{T}$ cm^6/mol^2-s	$M = F_2$
		$k = \frac{2.2x10^{-29}}{T}$ cm^6/mol^2-s	M = HF
		$k = \frac{4.4x10^{-29}}{T}$ cm^6/mol^2-s	M = F

Table 1.- Continued

21.	$H + OH + M \rightarrow H_2O + M$		
Ref.	Kinetic Methods	Rate Data	Comments
9 Bahn, et. al. (1969)	Recommeneded rate constants	rate = $k[H][OH][M]$	T in ^oK
		$k = \frac{8.3x10^{-29}}{T}$ cm^6/mol^2-s	$M = F_2$
		$k = \frac{3.3x10^{-28}}{T}$ cm^6/mol^2-s	M = F
		$k = \frac{1.7x10^{-28}}{T}$ cm^6/mol^2-s	M = HF
22.	$O + O + M \rightarrow O_2 + M$		
9 Bahn, et. al. (1969)	Recommended rate constants	rate = $k[O]^2[M]$	T in ^oK
		$k = \frac{3.3x10^{-31}}{T}$ cm^6/mol^2-s	$M = F_2$
		$k = \frac{1.3x10^{-30}}{T}$ cm^6/mol^2-s	M = F
		$k = \frac{6.6x10^{-30}}{T}$ cm^6/mol^2-s	M = HF
23.	$H + H + M \rightarrow H_2 + M$		
9 Bahn, et. al. (1969)	Recommended rate constants	rate = $k[H]^2[M]$	T in ^oK
		$k = \frac{2.8x10^{-30}}{T}$ cm^6/mol^2-s	$M = F_2$
		$k = \frac{1.1x10^{-29}}{T}$ cm^6/mol^2-s	M = F
		$k = \frac{5.6x10^{-30}}{T}$ cm^6/mol^2-s	M = HF

Table 1.- Continued

24. $F_2 + 2NO + M \rightarrow 2FNO + M$

Ref.	Kinetic Methods	Rate Data	Comments
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: GC, MS, IR	$k = 7.75\times10^{-35}$ cm^6/mol^2-s	M = Ar R = radical Wall reactions accounted for Mechanism: 1) $F_2 + NO \rightarrow FNO + F$ 2) $F + NO + M \rightarrow FNO^* + M$ 3) $FNO^* \rightarrow FNO + h\nu$ 4) $FNO^* + M \rightarrow FNO + M$ 5) $F + R\text{-}X \rightarrow XF + R$ 6) $R + NO \rightarrow RNO$ 7) $R + F_2 \rightarrow RF + F$ 8) $R + FNO \rightarrow RF + NO$ 9) $R + F \rightarrow RF$ 10) $R + R \rightarrow R_2$
80 Johnston, et. al. (1959)	Steady flow system Calorimeter T = 294.5 = 299.5 °K	$\Delta H^{o}{}_{298^{o}K} = -74.8$ kcal.mole $\Delta H_f(FNO) = -15.8$ kcal/mole $D(F\text{-}NO) = 55.4$ kcal/mole Step 1: ΔH^{o}_{298} $^{o}K = -19.4$ kcal/mole Step 4: ΔH^{o}_{298} $^{o}K = -55.4$ kcal/mole	Reaction as chemiluminescent Mechanism: 1) $NO + F_2 \rightarrow FNO + F$ 2) $NO + F \rightleftarrows FNO^*$ 3) $FNO^* \rightarrow FNO + h\nu$ 4) $NO + F + M \rightarrow FNO + M$

Table 1.- Continued

24.	$F_2 + 2NO + M \rightarrow 2FNO + M$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
121 Rapp, et. al. (1960)	$T = 195\text{-}300^oK$ Dilute diffusion flame method Product analysis: Photographic (visible)	$E_{a,1} = 1.5 \pm 1.0$ kcal/mole $A_1 = 1x10^{-12}$ $cm^3/mol\text{-}s$	Mechanism: 1) $NO + F_2 \rightarrow ONF$ (rate determining step) 2) $NO + F \rightarrow ONF^*$ 3) $ONF^* \rightarrow ONF + h\nu$ 4) $ONF^* + M \rightarrow ONF$
25.	$F_2O + FNO_3 \rightarrow F_2 + FNO_2 + O_2$		
24 Bruna, et. al. (1972)	$T = 298^oK$ Photolytic reaction; O_2 inhibition $\lambda = 3650$ Å	For $F_2NO_3 \rightarrow FO + FNO_3$, $A = 10^{14}s^{-1}$ At 298^oK, $k = 4.8x10^{-8}$ s^{-1} At 307^oK, $k = 1.8x10^{-7}$ s^{-1} At 317^oK, $k = 9.1x10^{-7}$ s^{-1}	Mechanism: 1) $F_2O + h\nu \rightarrow F + FO$ 2) $FO + FNO_3 \rightarrow FNO_2 + F + O_2$ 3) $F + F + M \rightarrow F_2 + M$ 4) $FO + FNO_3 \rightleftarrows F_2NO_3$ (unbalanced) 5) $FO + F_2NO_3 \rightarrow FNO_2 + F_2 + O_2$
26.	$F_2O + NOF \rightarrow NO_2F + F_2$		
24 Bruna, et. al. (1972)	$\lambda = 3650$ Å $T = 298$ ^oK	Quantum yield < 1 and depends on $[NO_2F]$	NO_2F has an inhibiting effect on the rate

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
27.	$2FNO_3 \rightarrow 2FNO_2 + O_2$		
140 Skiens, et. al. (1958)	$T = 373^oK$ Thermal reaction Product analysis: IR, MS, gas density	$k_\infty = 5.80\times10^{13} \exp\left(\frac{29700}{RT}\right)\ s^{-1}$ At $T = 353^oK$, $\tau_{1/2} = 7$ hours $D(F\text{-}NO_2) = 29.7$ kcal/mole $E_{a,\ 2} \cong 8$ kcal/mole Mechanism changes with added NO_2 Reaction becomes: $FNO_3 + NO_2 \rightarrow FNO_2 + NO_3$	Explosive at low pressures Mechanism: 1) $FNO_3 \rightarrow F + NO_3$ (rate determining step) 2) $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$ 3) $NO_2 + F + M \rightarrow FNO_2 + M$ Mechanism: 2) $NO_3 + NO_2 \rightarrow NO_2 + NO + O_2$ 3) $NO_3 + NO \rightarrow 2NO_2$ 4) $2NO + O_2 \rightarrow 2NO_2$
138 Sicre, et. al. (1962)	Thermal reaction $T = 363 - 383\ ^oK$ F_2 catalyzed decomposition	$A = 1.11\times10^{-9}\ cm^3/mol\text{-}s$ $E_a = 22.7$ kcal/mole	Mechanism: 1) $FNO_3 \rightarrow F + NO_3$ 2) $NO_3 + F_2 \rightarrow NO_2F + OF$ 3) $OF + NO_3F \rightarrow \frac{1}{2} F_2 + FNO_2 + \frac{1}{2} O_2$
28.	$F_2 + 2NO_2 \rightarrow 2FNO_2$		
113 Perrine, et. al. (1953)	$T = 300.9^oK,\ 323.6\ ^oK,\ 343.4\ ^oK$ Product analysis: optical, absorptiometric	rate $= k[NO_2][F_2]$ $A = 2.7\times10^{-12}\ cm^3/mol\text{-}s$ $E_a = 10.47\pm0.18$ kcal/mole	Mechanism: 1) $NO_2 + F_2 \rightarrow F + FNO_2$ 2) $NO_2 + F + M \rightarrow FNO_2 + M$

Table 1.– Continued

Ref.	Kinetic Methods	Rate Data	Comments
28.	$F_2 + 2NO_2 \rightarrow 2FNO_2$ (continued)		
141 Smardzewski, et. al. (1974)	λ = 2300-4000 Å Cryogenic matrix study T = 4°K Product analysis: IR , Raman of OF and OF_2	Net reaction: $F_2 + NO_2 \rightarrow NO + OF_2$	Mechanism: 1) $F_2 + h\nu \rightarrow 2F$ 2) $NO_2 + h\nu \rightarrow NO + O$ 3) $O + F \rightarrow OF$ 4) $OF + F \rightarrow OF_2$ 5) $O + F_2 \rightarrow OF_2$ 6) $OF + h\nu \rightarrow OF + F$
29.	$F_2 + N_2O \rightarrow OF_2 + N_2$		
112 Ogden, et. al. (1967)	T = 4°K Photolysis source: Hg lamp Product detection: IR	$D(O-F) \geqq 40$ kcal/mole	Mechanism: 1) $F + N_2O \rightarrow OF + N_2$ 2) $OF + F \rightarrow OF_2$ 3) $OF + F_2 \rightarrow OF_2 + F$
30.	$NF_2 + F + M \rightarrow NF_3 + M$		
32 Clyne, et. al. (1974)	Discharge flow system Product analysis: MS	$\Delta U^{o}_{298} = -60.5$ kcal/mole $k_{298^{o}K} = (8.9 \pm 3.3) \times 10^{-31}$ cm^6/mol^2-s	
31.	$O_2(a^1\Delta) + NF(a^1\Delta) \rightarrow O_2(X^3\Sigma^-) + NF(b^1\Sigma^+)$		
71 Herbelin, et. al. (1973)	Radio frequency descharge	$k \cong 2 \times 10^{-12}$ cm^3/mol-s	

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Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
32.	$NF_2(^2B_1) + H \rightarrow HF(v - 2) + NF(b^1\Sigma^+)$		
71 Herbelin, et. al. (1973)	Radio frequency discharge flow system	$k \cong 2 \times 10^{-13}$ cm^3/mol-s	Mechanism: $NF_2(^2B_1) + H \rightarrow HF^* + NF(a^1\Delta)$ $HF(v \geq 2) + NF(a^1\Delta) \rightarrow$ $HF(v - 2) + NF(b^1\Sigma^+)$ Efficient quenchers of HF^*: HF(0), CO_2, NO Inefficient quenchers of HF^*: $NF(a^1\Delta)$
33.	$F + NH_3 \rightarrow HF + NH_2$		
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: GC, MS, IR	$k = 5.5 \times 10^{-13}$ cm^3/mol-s	
34.	$FO + FO \rightarrow 2F + O_2$		
32 Clyne, et. al. (1974)	T = 298°K Discharge flow system Product analysis: MS	$\Delta U^o_{298^oK} = -16.3$ kcal/mole $k_{298^oK} = (8.5 \pm 2.8) \times 10^{-12}$ cm^3/mol-s	
35.	$F + O_3 \rightarrow OF + O_2$		
151 Wagner, et. al. (1972)	Product analysis: MS of OF F from microwave discharge Flow system	$A = 2.8 \times 10^{-11} cm^3$/mol-s $E_a = 450$ cal/mole	Intermediate reaction: $OF^* + OF \rightarrow 2F + O_2$ $k \cong 3.3 \times 10^{-11} cm^3$/mol-s

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
35.	$F + O_3 \rightarrow OF + O_2$ (continued)		
149 Wagner, et. al. (1971)	T = 298°K F atoms produced by microwave discharge Product analysis: MS of OF	$k_{298^\circ K} \cong 8.3 \times 10^{-12} cm^3/mol\text{-}s$	Subsequent rapid reaction is: $N + OF \rightarrow NO + F$
142 Staricco, et. al. (1962)	T = 273 - 293°K λ = 5760 Å	Quantum yield at 293°K = 4.6×10^3 mol/photon $E_a \cong 3$ kcal/mole Temperature coefficient = 1.19/10° rise $-\frac{d[O_3]}{dt} = k\ J_{abs}$	Observed product is $O(^3P)$ Reaction 35 is at least 4 times slower than $F + O_3 \rightarrow F + O_2 + O(^3P)$ Long chain lengths postulated.
137 Sicre, et. al. (1958)	T = 318 - 338°K Thermal reaction P = 15-400 torr	Temperature coefficient = 2.0/10° rise	Wall reactions important F atoms react with decomposition products at O_3: $O_3 \rightarrow O + O_2^*$
36.	$F_2O + 2F_2SO \rightarrow F_4SO + F_2SO_2$		
27 Castellano, et. al. (1964)	T = 278 = 293°K λ = 3650 Å	Quantum yield = 1.0 mol/hν	Rate is: a) independent of reactant concentration b) independent of oxygen concentration c) independent of temperature No thermal reaction occurs Mechanism: 1) $F_2O + h\nu \rightarrow F + FO$ 2) $F + F_2SO \rightarrow F_3SO$ 3) $F_2SO + FO \rightarrow F_2SO_2 + F$ 4) $2F_3SO \rightarrow F_4SO + F_2SO$

Table 1.- Continued

37.	$F_2 + F_2SO \rightarrow F_4SO$		
Ref.	Kinetic Methods	Rate Data	Comments
27 Castellano, et. al. (1964)	$\lambda = 3650$ Å $T = 278 - 293$ °K	At $T = 293$°K. thermal reaction is 20% of photolytic reaction For: $P_{F_2} < 30$ torr, $\Phi = 1.0$ mol/photon $P_{F_2} = 250$ torr, $T = 278$ °K, $\Phi = 1.12$ mol/photon $P_{F_2} = 250$ torr, $T = 293$ °K, $\Phi = 1.28$ mol/photon	Mechanism: 1) $F_2 \rightarrow 2F$ 2) $F + F_2SO \rightarrow F_3SO$ 3) $F_3SO + F_2 \rightarrow F_4SO + F$ 4) $2F_3SO \rightarrow F_4SO + F_2SO$
148 Vallana, et. al. (1964)	$T = 323 - 393$°K Thermal reaction	Activation energies for steps in mechanism: $E_{a,1} = 12.0$ kcal/mole $E_{a,3} = 18.0$ kcal/mole $E_{a,4} = 9.8$ kcal/mole $E_{a,5} = 0$	Independent of pressure Mechanism: 1) $F_2SO + F_2 \rightarrow F_3SO + F$ 2) $F + F_2SO \rightarrow F_3SO$ 3) $2F_2SO + F_2 \rightarrow 2F_3SO$ 4) $F_3SO + F_2 \rightarrow F_4SO + F$ 5) $2F_3SO \rightarrow F_4SO + F_2SO$
38.	$CO + O + M \rightarrow CO_2 + M$		
98 Mahan, et. al. (1961)	High pressure limit	$k = 8\times10^{-15} \exp\left(-\frac{3700}{RT}\right)$ cm^3/mol-s	

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
38.	$CO + O + M \rightarrow CO_2 + M$ (continued)		
139 Simonaitis, et. al. (1972)	$\lambda \geqq 2200$ Å N_2O diluent gas Product analysis: GC	High pressure: $A_\infty = 2.66 \times 10^{-14}$ cm^3/mol-s $E_{a\infty} = 2900$ cal/mole Low pressure: $A_o = 1.63 \times 10^{-32}$ cm^6/mol^2-s $E_{a,0} = 4100$ cal/mole $k_o = k_1$ $k_\infty = \frac{k_1 k_2}{k_{-1}}$	Mechanism: 1) $O(^3P) + CO + M \rightleftarrows CO_2(^3B_2) + M$ 2) $CO_2(^3B_2) \rightleftarrows CO_2(^1B_2)$ 3) $CO_2(^1B_2) + M \rightarrow CO_2(^1\Sigma_g^+) + M$
39.	$CO + OH \rightarrow CO_2 + H$		
156 Wilson (1972)		$A = 5.1 \times 10^{-13}$cm^3/mol-s $E_a = 596$ cal/mole	
40.	$F + CO_2 + M \rightarrow CF_3OF + \frac{1}{2} O_2 + M$		
86 Jubert, et. al. (1969)	$T = 353 - 408^\circ K$ Photochemical reaction $\lambda = 3130, 3650$ Å Product analysis: IR, UV, visible	Quantum yield < 0.1 mol/photon $E_{a,2} = 10.9 \pm 0.3$ kcal/mole $D(FO-C) = 14 \pm 2$ kcal/mole third body — efficiency F_2 — 1.0 O_2 — 1.0 N_2 — 1.0 CO_2 — 1.5 CF_3OF — 2.0 SiF_4 — 2.0 CF_4 — 6.5	Mechanism: 1) $F_2 + h\nu \rightarrow 2F$ 2) $F + CO_2 + M \rightarrow FCO_2 + M$ 3) $FCO_2 + F \rightarrow CF_3OF + \frac{1}{2} O_2$ (unbalanced) 4) $FCO_2 + F_2 \rightarrow CF_3OF + \frac{1}{2} O_2$ (unbalanced) 5) $F + F + M \rightarrow F_2 + M$ 6) $F \xrightarrow{wall} SiF_4 + \frac{1}{2} O_2$ 7) $F + O_2 \rightleftarrows FO_2$ 8) $FO_2 + F \rightarrow F_2 + O_2$

Table 1.- Continued

41.	$F_2 + CO + O_2 \rightarrow COF_2 + CO + (FCO)_2O_2$		
Ref.	Kinetic Methods	Rate Data	Comments
70 Heras, et. al. (1961)	Thermal reaction Product detection: pressure measurements $T = 288 - 318^{\circ}K$	$-\frac{dP}{dt} = k(F_2)(CO)$ $A_{rds} = 7.8 \times 10^{-13}$ cm^3/mol-s $E_{a,rds} = 13500 \pm 1200$ cal/mole Steric factor: $\alpha = 2.8 \times 10^{-3}$ Temperature coefficient = 2.10/10° rise	$F_2 + CO \rightarrow FCO + F$ (rate determining step) Chain reaction mechanism
42.	$5CH_2O + 6\ O \rightarrow 3H_2 + 3CO + 2H_2O + 2CO_2 + O_2$		
72 Herron, et. al. (1969)	$T = 300^{\circ}K$ Flow system Product analysis: MS	$k_{300^{\circ}K} = (1.5 \pm 0.4) \times 10^{-13}$ cm^3/mol-s	Mechanism: 1) $O + CH_2O \rightarrow OH + CHO$ 2) $O + OH \rightarrow O_2 + H$ 3) $O + CHO \rightarrow CO + OH$ 4) $O + CHO \rightarrow CO_2 + H$ 5) $OH + CH_2O \rightarrow H_2O + CHO$ 6) $OH + OH \rightarrow H_2O + O$ 7) $H + CH_2O \rightarrow H_2 + CHO$ 8) $H + CHO \rightarrow H_2 + CO$
43.	$CH_2 + OH \rightarrow CHO + H_2O$		
111 Morris, et. al. (1971)	$T = 353^{\circ}K$ Discharge flow system Product analysis: MS Photolytic reaction	$k = 1.4 \times 10^{-11}$ cm^3/mol-s	Error in rate data = ± 25%

Table 1.- Continued

44.	$CF_2O + F_2 \rightarrow CF_3OF + CF_3OOCF_3$		
Ref.	Kinetic Methods	Rate Data	Comments
96 Lopez, et. al. (1974)	T = 288 - 353°K λ = 3650 Å $I_o = 1x10^{19}$ At T = 303°K, $\epsilon_{F_2} = 6.61x10^{-5}$ torr^{-1}	$\Phi_{CF_2O} = \frac{2[CF_2O]}{k + [CF_2O]}$ Quantum yield $\leq$ 2 mol/photon $E_{a,2}$ = 6.2 kcal/mole $E_{a,6}-E_{a,4}$ = 5 kcal/mole $E_{a,8} = 0$ $E_{a,9} = 0$ $E_{a,9'} \cong 11 \pm 3$ kcal/mole $E_{a,10} \cong 3$ kcal/mole	Mechanism without O_2 inhibition: 1) $F_2 + h\nu \rightarrow 2F$ 2) $F + CF_2O \rightarrow CF_2OF$ 3) $2CF_2OF \rightarrow (CF_2OF)_2^*$ 4) $(CF_2OF)_2^* \rightarrow (CF_2OF)_2'$ 5) $(CF_2OF)_2^* \xrightarrow{wall} CF_3OF + CF_2O$ 6) $(CF_2CF)_2^* + CF_2O \rightarrow (CF_3O)_2 + CF_2O$ 7) $(CF_2OF)_2' \rightarrow 2CF_3OF$ (unbalanced) 8) $F \xrightarrow{wall} \frac{1}{2} F_2$ 9) $F + O_2 \rightleftarrows FO_2$ 10) $F + FO_2 \rightarrow F_2 + O_2$ No thermal reaction occurs
45.	$2CH_3O_2 \rightarrow 2CH_3O + O_2$		
93 Levy (1972)	T = 283°K λ = 3130 Å	k = 2 x 10^{-15} cm^3/mol-s	
46.	$CH_3O + O_2 \rightarrow CH_2O + HO_2$		
67 Heicklen, et. al. (1968)	Estimated rate data	A = 1.7 x 10^{-13} cm^3/mol-s E_a = 6360 cal/mole	

Table 1.- Continued

Ref.	Kinetic Method	Rate Data	Comments
47.	$CH_3O + NO \rightarrow CH_2O + HNO$		
102 McGraw, et. al. (1969)	λ = 3660 Å Flow system $I_o = 6.0 \times 10^{15}$ photons/cm^3-s	$k = 1.0 \times 10^{-14}$ cm^3/mol-s	
48.	$CH_3O + NO_2 \rightarrow CH_3ONO_2$		
68 Heicklen, et. al.(1968)		$k - 1.0 \times 10^{-13}$ cm^3/mol-s	
49.	$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$		
87 Kerr, et. al. (1965)	λ = 3660 Å Product analysis:	$\Delta H_f^o(CH_3CO) = -3.1$ kcal/mole $k_8 = 3.6 \times 10^{-11}$ cm^3/mol-s $A_9 = 5.25 \times 10^{-13}$ cm^3/mol-s $E_{a,9} \simeq 6800$ cal/mole $A_{10} \simeq 3.0 \times 10^{-13}$ cm^3/mol-s $E_{a,10} \simeq 7100$ cal/mole Assumed: k_8	$M = CO, (CH_3)_2N_2, n\text{-}C_5H_{10}$ Mechanism: 1) $(CH_3)_2N_2 + h\nu \rightarrow 2CH_3 + N_2$ 2) $CH_3 + CO \rightarrow CH_3CO^*$ 3) $CH_3CO^* \rightarrow CH_3 + CO$ 4) $CH_3CO^* + M \rightarrow CH_3CO + M$ 5) $CH_3CO + M \rightarrow CH_3CO^* + M$ 6) $CH_3CO + CH_3 \rightarrow CH_3COCH_3$ 7) $2CH_3CO \rightarrow (CH_3CO)_2$ 8) $2CH_3 \rightarrow C_2H_6$ 9) $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$ 10) $CH_3 + (CH_3)_2N_2 \rightarrow (CH_3)_2^*NNCH_3$
50.	$M + CH_3 + O_2 \rightarrow CH_3O_2 + M$		
67, Heicklen, et. al.(1968)	Estimated rate data	$k = 8 \times 10^{-32}$ cm^6/mol^2-s	

Table 1.- Continued

51.	$CH_4 + OH \rightarrow CH_3 + H_2O$		
Ref.	Kinetic Methods	Rate Data	Comments
156 Wilson (1972)	Review of rate data	$A = 4.8 \times 10^{-11}$ cm^3/mol-s E_a = 4970 cal/mole	
157 Wilson, et. al. (1967)	OH produced from $H + HNO_2$ Fast flow reactor Product analysis: ESR	$A = 4.8 \times 10^{-11}$ cm^3/mol-s E_a = 5000 cal/mole	Mechanism: (1) $CH_4 + OH \rightarrow CH_3 + H_2O$ (2) $CH_3 + OH \rightarrow H_2CO + H_2$ (3) $CH_3 + O_2 \rightarrow H_2CO + OH$ (4) $H_2CO + OH \rightarrow HCO + H_2O$ (5) $H_2CO + H \rightarrow HCO + H_2$ (6) $HCO + OH \rightarrow CO + H_2O$ (7) $HCO + H \rightarrow CO + H_2$
52.	$O + CH_4 \rightarrow OH + CH_3$		
65 Harteck, et. al. (1931)		$A = 10^{-10}$ cm^3/mol-s E_a = 7 kcal/mole	Assumed

Table 1.- Continued

52. $O + CH_4 \rightarrow OH + CH_3$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
61 Greenberg, et. al. (1972)	Photolysis of N_2O at λ = 2139 Å to produce $O(^1D)$ T = 298°K Product analysis: GC P = 10-100 torr	For translationally energetic $O(^1D)$: $\frac{k_{1-5}}{k_6 + k_7} = 2.28 \pm 0.20$ For no excess translational energy: $\frac{k_{1-5}}{k_6+k_7} = 1.35 \pm 0.30$	Mechanism: (1) $O(^1D) + CH_4 \rightarrow HO + CH_3$ (2) $HO + CH_4 \rightarrow H_2O + CH_3$ (3) $2CH_3 \rightarrow C_2H_6$ (4) $HO + CH_3 \rightarrow CH_3OH$ (5) $O(^1D) + CH_4 \rightarrow CH_3OH$ (6) $O(^1D) + N_2O \rightarrow N_2 + O_2$ (7) $O(^1D) + N_2O \rightarrow 2NO$ Rates measured relative to reactions 6 and 7 where $k_6 + k_7 = 1.8 \times 10^{-10}$ cm^3/mol-s from reference 202. Important of reactions: $O(^1D) + CH_4 \rightarrow HO + CH_3$ 95± 5% $O(^1D) + CH_4 \rightarrow O(^3P) + CH_4$ 5 ± 5% $O(^1D) + CH_4 \rightarrow CH_2 + H_2O$ <3% $O(^1D) + CH_4 \rightarrow CH_3OH$ <1% $O(^1D) + CH_4 \rightarrow CH_2O + H_2$ <0.2%
153 Westenberg, et. al. (1969)	T = 500 - 900°K Fast flow reactor Product analysis: ESR	$A = 3.3 \times 10^{-11}$ cm^3/mol-s E_a = 9200 cal/mole	

Table 1.- Continued

53. $CH + H_2S \rightarrow CH_4 + SH$

Ref.	Kinetic Methods	Rate Data	Comments
77 Imai, et. al. (1960)	Photolysis of CH_3OCH_3 to produce CH_3 $T = 323 - 413^{\circ}K$ Product analysis: gas burette, derivative preparation	$A = 4.2 \times 10^{-13}$ cm^3/mol-s $E_a = 2600$ cal/mole	Mechanism: (1) $CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$ (2) $CH_3CO \rightarrow CH_3 + CO$ (3) $2CH_3 \rightarrow C_2H_6$ (4) $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2$ (5) $CH_3 + H_2S \rightarrow CH_4 + SH$
78 Imai, et. al. (1960)	Photolysis of CH_3CHO to produce CH_3 $T = 423 - 633^{\circ}K$ Product detection: pressure measurements	$\frac{A_2}{A_1} = 1.7 \pm 0.5$ $E_1 - E_2 = 4.0$ kcal/mole	Rate measured relative to: (1) $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$ (2) $CH_3 + H_2S \rightarrow CH_4 + SH$ Mechanism: (1) $CH_3CHO + h\nu \rightarrow CH_3 + CHO$ (2) $CHO \rightarrow CO + H$ (3) $H + CH_3CHO \rightarrow H_2 + CH_3CO$ (4) $CH_3CO \rightarrow CH_3 + CO$ (5) $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$ (6) $2CH_3 \rightarrow C_2H_6$ (7) $CH_3 + H_2S \rightarrow CH_4 + SH$ (8) $SH + CH_3CHO \rightarrow H_2S + CH_3CO$

Table 1.- Continued

54. $CF_3 + H_2S \rightarrow CHF_3 + SH$

Ref.	Kinetic Methods	Rate Data	Comments
4 Arthur, et. al. (1966)	Product analysis: GC Vacuum system λ = 100 - 275 Å Photolysis of $(CF_3)_2CO$ to produce CF_3	$A = (7.7 \pm 1.1) \times 10^{-14}$ $cm^3/mol\text{-}s$ E_a = 3880±260 cal/mole $E_{a,2} = 0$ assumed	Measured relative to recombination rate constant for CF_3 Mechanism: (1) $(CF_3)_2CO + h\nu \rightarrow 2CF_3 + CO$ (2) $2CF_3 \rightarrow C_2F_6$ (3) $CF_3 + H_2S \rightarrow CHF_3 + SH$ (4) $2SH \rightarrow H_2 + S_2$ (5) $2SH \rightarrow H_2S + S$

55. $6CF_3 + 3CH_4 \rightarrow C_2H_6 + C_2F_6 + CF_3CH_3 + 3CHF_3$

Ref.	Kinetic Methods	Rate Data	Comments
7 Ayscough, et. al. (1955)	λ = 3000 - 3200 Å Rotating sector technique Product analysis: IR	At $T = 400^\circ K$, $k_5 = 3.88 \times 10^{-11}$ $cm^3/mol\text{-}s$ $E_2 \geq 1.5$ kcal/mole $k_2 = 9.3 \times 10^{-11}$ $cm^3/mol\text{-}s$ $\frac{k_3}{k_2^{1/2}} = 7.7 \times 10^{-7} \exp\left(-\frac{(10300 \pm 500)}{RT}\right) cm^{3/2}/mol^{1/2}\text{-}s$	Mechanism: (1) $CF_3COCF_3 + h\nu \rightarrow 2CF_3 + CO$ (2) $2CF_3 \rightarrow C_2F_6$ (3) $CF_3 + CH_4 \rightarrow CHF_3 + CH_3$ (4) $CF_3 + CH_3 \rightarrow CF_3CH_3$ (5) $2CH_3 \rightarrow C_2H_6$

Table 1.- Continued

55. $6CF_3 + 3CH_4 \rightarrow C_2H_6 + C_2F_6 + CF_3CH_3 + 3CHF_3$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
2 Alcock, et. al. (1965)	Photolysis of $(CF_3)_2CO$ to produce CF_3 $\lambda > 2860$ Å Product analysis: GC T = 426 - 568°K	$E_4 = 0$ $\frac{k_3}{k_2^{1/2}} = (1.5 \pm 0.7)\times 10^{-7} \exp\left(-\frac{(11300 \pm 500)}{RT}\right)$ $cm^{3/2}/mol^{1/2}-s^{1/2}$	Assumed Mechanism of reference 9 (above) 6) $CF_3 + CH_3Cl \rightarrow CHF_3 + CH_2Cl$ 7) $CF_3 + CH_3Cl \rightarrow CClF_3 + CH_3$ 8) $CF_3 + CH_3Br \rightarrow CHF_3 + CH_2Br$ 9) $CF_3 + CH_3Br \rightarrow CBrF_3 + CH_3$ 10) $CF_3 + CH_3I \rightarrow CHF_3 + CH_2I$ 11) $CF_3 + CH_3I \rightarrow CIF_3 + CH_3$
	T = 417 - 673°K	Low pressure competition reactions $\frac{k_6}{k_2^{1/2}} = (2.1 \pm 0.4) \times 10^{-6} \exp\left(-\frac{(10600 \pm 200)}{RT}\right)$ $cm^{3/2}/mol^{1/2}-s^{1/2}$	
	T = 423-533 °K No photolytic products	$\frac{k_6}{k_7} \geqq 2000$ $\frac{k_8}{k_2^{1/2}} = (2.5 \pm 0.8) \times 10^{-6} \exp\left(-\frac{(10900 \pm 300)}{RT}\right)$ $cm^{3/2}/mol^{1/2}-s^{1/2}$ $\frac{k_9}{k_2^{1/2}} = (1.1 \pm .5) \times 10^{-7} \exp\left(-\frac{(8400 \pm 100)}{RT}\right)$ $cm^{3/2}/mol^{1/2}-s^{1/2}$	

Table 1.- Continued

55.	$6CF_3 + 3CH_4 \rightarrow C_2H_6 + C_2F_6 + CF_3CH_3 + 3CHF_3$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
2 (continued)	T = 328 - 483°K	$\frac{k_8}{k_9} = (22 \pm 6) \exp\left(-\frac{(2500 \pm 250)}{RT}\right)$ $\frac{k_{10}}{k_2^{1/2}} = (7.0 \pm 2.5) \times 10^{-8} \exp\left(\frac{-(7500 \pm 300)}{RT}\right) cm^{3/2}/mol^{1/2}\text{-}s^{1/2}$ $\frac{k_{11}}{k_2^{1/2}} = (6.2 \pm 1.2) \times 10^{-9} \exp\left(\frac{-(3300 \pm 150)}{RT}\right) cm^{3/2}/mol^{1/2}\text{-}s^{1/2}$ $\frac{k_{10}}{k_{11}} = (28 \pm 11) \exp\left(\frac{-(4900 \pm 300)}{RT}\right)$	
8 Ayscough, et. al. (1955)	T = 353 - 573°K λ = 3130 Å Product analysis: gas burette, MS, IR	$\frac{k_3}{k_2^{1/2}} = 1.29 \times 10^{-8} \exp\left(\frac{-(10300 \pm 500)}{RT}\right)$	Relative rate measured using mechanism of references 2 and 9.
56.	$CF + F + M \rightarrow CF_2 + M$		
110 Modica, et. al. (1968)	T = 1700 - 3000°K Shock tube Product analysis: UV	$k = \frac{1.8 \times 10^{-21}}{T^{2.85}} cm^6/mol^2\text{-}s$	M = Ar

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
57.	$O + C_2H_4 \rightarrow CH_2O + CH_4 + CH_3CHO + CO + H_2 + O_2$		
72 Herron, et. al. (1969)	Low pressure Flow system Product analysis: MS	Steps 6-8 originally proposed in reference 191. From reference 192: $k_7 = 6.3 \times 10^{-12} cm^3/mol\text{-}s$ $k_8 = 3.6 \times 10^{-11}\ cm^3/mol\text{-}s$ From reference 193: $k_2 = (3.2 \pm 0.5) \times 10^{-11}\ cm^3/mol\text{-}s$	Clarification of mechanism: 1) $O + C_2H_4 \rightarrow CH_3 + CHO$ 2) $O + CH_3 \rightarrow CH_2O + H$ 3) $O + CHO \rightarrow CO + OH$ 4) $O + OH \rightarrow O_2 + H$ 5) $O + CH_2O \rightarrow OH + CHO$ 6) $H + HCO \rightarrow H_2 + CO$ 7) $CH_3 + CHO \rightarrow CH_3CHO$ 8) $CH_3 + CHO \rightarrow CH_4 + OH$
37 Davis, et. al. (1972)	$T = 232 - 500^{\circ}K$ $\lambda = 1759$ Å Flask photolysis-resonance fluorescence technique	$A = (5.42 \pm 0.30) \times 10^{-12}\ cm^3/mol\text{-}s$ $E_a = 1130 \pm 32$ cal/mole	
58.	$4\ O(^3P) + 4C_2F_4 \rightarrow 3CF_2O + 2\,^1CF_2 + C_2F_4O^* + CF_2O_2$		
146 Tyerman, et. al. (1969)	$\lambda > 3000$ Å Flash photolysis Product analysis: IR	$k = 5 \times 10^4\ s^{-1}$	
81 Johnston, et. al. (1967)	$\lambda \geq 2200$ Å Product detection: IR of CF_2O	Quantum yield of CF_2O = 1.0 mol/photon $\frac{k_3}{k_4^{1/2}} = 5.0 \times 10^{-10}\ cm^{3/2}/mol^{1/2}\text{-}s^{1/2}$	Mechanism: 1) $O(^3P) + C_2F_4 \rightarrow CF_2O + {}^3CF_2$ 2) $O(^3P) + C_2F_4 \rightarrow C_2F_4O^*$ 3) ${}^3CF_2 + O_2 \rightarrow CF_2O_2$ 4) $2\,{}^3CF_2 \rightarrow C_2F_4{}^*$

Table 1.- Continued

Ref.	Kinetic Method	Rate Data	Comments
59.	$O(^3P) + CF_2{=}CFCl \rightarrow CF_2O + CFClO + CF_2 + CFCl$		
146 Tyerman, et. al., (1969)	Flash photolysis of O_2 to produce $O(^3P)$ $\lambda > 3000$ Å Product analysis: IR	$A = 3.9 \times 10^{-11}$ cm^3/mol-s $E_a = 2.61$ kcal/mole	Rate measured relative to the rate of $O(^3P) + C_2F_4$
60.	$O(^3P) + CF_2{=}CCl_2 \rightarrow CF_2O + CCl_2O + CF_2 + CCl_2$		
146 Tyerman, et. al. (1969)	Flash photolysis of O_2 to produce $O(^3P)$ $\lambda > 3000$ Å Product analysis: IR	$A = 5.7 \times 10^{-12}$ cm^3/mol-s $E_a = 1.29$ kcal/mole	Rate measured relative to the rate of $O(^3P) + C_2F_4$
61.	$F_2 + O_2 + CCl_2{=}CCl_2 \rightarrow CCl_2FCOCl + CCl_3COCl + CCl_2O$		
104 Miller, et. al. (1956)	Product analysis: derivatives made and characterized	When $\frac{[O_2]}{[F_2]} = 2.8$, $[CCl_2FCOCl] : [CCl_3COCl] : [CCl_2O] = 1.0 : 4.5 : 1.5$ When $[O_2] : [F_2] = 4.7$, $[CCl_2FCOCl] : [CCl_3COCl] : [CCl_2O] = 1.0 : 3.0 : 0.40$	Non-gaseous products Mechanism: 1) $CCl_2{=}CCl_2 + F_2 \rightarrow CCl_2FCCl_2 + F$ 2) $CCl_2{=}CCl_2 + F \rightarrow CCl_2FCCl_2$ 3) $CCl_2FCCl_2 + O_2 \rightarrow CCl_2FCCl_2O_2$ 4) $CCl_2FCCl_2O_2 \rightarrow CCl_2FCOCl + ClO$ 5) $CCl_2{=}CCl_2 + ClO \rightarrow CCl_3COCl + Cl$ 6) $CCl_2FCCl_2O_2 \rightarrow CCl_2FCOCl + ClO$ 7) $CCl_2FCCl_2O_2 \rightarrow 2CCl_2O + F$

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
62.	$3CH_2{=}CH_2 + 5CCl_3Br \rightarrow CCl_3CH_2CH_2Br + 2CCl_3CCl_3 + 2CH_2BrCH_2Br$		
144 Tedder, et. al. (1966)	Rotating sector technique $\lambda > 2800$ Å Product analysis: gas density	$A = 6.6 \times 10^{-16}$ cm^3/mol-s $E_a = 3200 \pm 300$ cal/mole	1) $CCl_3Br + h\nu \rightarrow CCl_3 + Br$ 2) $CCl_3 + CH_2{=}CH_2 \rightarrow CCl_3CH_2CH_2$ 3) $CCl_3CH_2CH_2 + CCl_3Br \rightarrow CCl_3CH_2CH_2Br + CCl_3$ 4) $CCl_3 + CCl_3 \rightarrow C_2Cl_6$ 5) $Br + CH_2{=}CH_2 \rightarrow CH_2CH_2Br$ 6) $CH_2CH_2Br + CCl_3Br \rightarrow CH_2BrCH_2Br + CCl_3$
63.	$3CHF{=}CH_2 + 5CCl_3Br \rightarrow CCl_3CHFCH_2Br + 2CCl_3CCl_3 + 2CHFBrCH_2Br$		
144 Tedder, et. al. (1966)	Product analysis: gas density $\lambda > 2800$ Å Rotating sector technique	$A = (4.18 \pm 0.16) \times 10^{-16}$ cm^3/mol-s $E_a = 5300 \pm 200$ cal/mole	Mechanism is identical to the mechanism of reaction 62.
64.	$3CH_2{=}CHF + 5CCl_3Br \rightarrow CCl_3CH_2CHFBr + 2CHFBrCH_2Br + 2CCl_3CCl_3$		
144 Tedder, et. al. (1966)	Product analysis: gas density $\lambda > 2800$ Å Rotating sector technique	$A = 5.27 \pm 0.19 \times 10^{-16}$ cm^3/mol-s $E_a = 3300 \pm 200$ cal/mole	Mechanism is identical to the mechanism of reaction 62.
65.	$3CH_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CH_2CF_2Br + 2CH_2BrCF_2Br + 2CCl_3CCl_3$		
144 Tedder , et. al. (1966)	Product analysis: gas density $\lambda > 2800$ Å Rotating sector technique	$A = (8.4 \pm 0.4) \times 10^{-16}$ cm^3/mol-s $E_a = 4600 \pm 300$ cal/mole	Mechanism is identical to the mechanism of reaction 62.

Table 1.- Continued

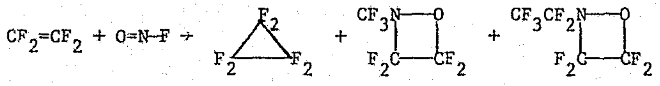
Ref.	Kinetic Methods	Rate Data	Comments
66.	$3CH_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CH_2Br + 2CH_2BrCF_2Br + 2CCl_3CCl_3$		
144 Tedder, et. al. (1966)	$\lambda > 2800$ Å Rotating sector technique Product analysis: gas density	$A = (5.3 \pm 0.3) \times 10^{-16}\ cm^3/mol\text{-}s$ $E_a = 8300 \pm 500$ cal/mole	Mechanism is identical to the mechanism of reaction 62.
67.	$3CHF{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CHFCF_2Br + 2CHFBrCF_2Br + 2CCl_3CCl_3$		
144 Tedder, et. al. (1966)	$\lambda > 2800$ Å Rotating sector technique Product analysis: gas density	$A = (3.3 \pm 0.2) \times 10^{-15}\ cm^3/mol\text{-}s$ $E_a = 6100 \pm 800$ cal/mole	Mechanism is identical to the mechanism of reaction 62.
68.	$3CHF{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CHFBr + 2CHFBrCF_2Br + 2CCl_3CCl_3$		
144 Tedder, et. al. (1966)	$\lambda > 2800$ Å Rotating sector technique Product analysis: gas density	$A = 4.2 \pm 0.3 \times 10^{-15}\ cm^3/mol\text{-}s$ $E_a = 7100 \pm 700$ cal/mole	Mechanism is identical to the mechanism of reaction 62.
69.	$3CF_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CF_2Br + 2CF_2BrCF_2Br + 2CCl_3CCl_3$		
144 Tedder, et. al. (1966)	$\lambda > 2800$ Å Rotating sector technique Product analysis: gas density	$A = 2.1 \pm 0.1 \times 10^{-14}\ cm^3/mol\text{-}s$ $E_a = 6100 \pm 400$ cal/mole	Mechanism is identical to the mechanism of reaction 62.
70.			
3 Andreades (1962)	UV photolysis Product analysis: VPC, IR, MS	$\Delta H_f^o(CF_2) = -17$ kcal/mole	Product analysis only A true insertion mechanism is not necessarily followed.

Table 1.- Continued

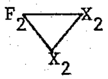
Ref.	Kinetic Methods	Rate Data	Comments
71.	$\frac{7}{2} F_2 + \frac{5}{2} Cl_2 + 6CCl_2{=}CCl_2 \rightarrow C_2Cl_6 + 2CCl_2FCCl_2F + 3CCl_2FCCl_3$		
105 Miller, et. al. (1956)	T = 152 °K Thermal reaction Product analysis: titration, derivative preparation and characterization		Mechanism: 1) $CCl_2{=}CCl_2 + F_2 \rightarrow CCl_2FCCl_2 + F$ 2) $CCl_2FCCl_2 + F \rightarrow CCl_2FCCl_2F$ 3) $CCl_2{=}CCl_2 + F \rightarrow CCl_2FCCl_2$ 4) $CCl_2FCCl_2 + Cl_2 \rightarrow CCl_2FCCl_3 + Cl$ 5) $CCl_2{=}CCl_2 + Cl \rightarrow CCl_3CCl_2$ 6) $CCl_3CCl_2 + Cl_2 \rightarrow CCl_3CCl_3 + Cl$ 7) $CCl_2FCCl_2 + F_2 \rightarrow CCl_2FCCl_2F + F$ 8) $CCl_3CCl_2 + F_2 \rightarrow CCl_3CCl_2F + F$
72.	 $\rightarrow CF_2 + CX_2{=}CX_2$		
15 Birchall, et. al. (1967)	T = 433 - 473 °K	X = Cl, F	Slow, quantitative thermal reaction Product observation
73.	$C_3H_8 + M \rightarrow CH_3 + C_2H_5 + M$		
58 Gawlowski, et. al. (1975)	λ = 1236.0 Å High pressure case Product analysis: MS	Quantum yield of $^3CH_2$ = 0.035 mol/photon	M = H_2S, NO Assumes $CH_2(^3P)$ and H_2S react Product identification only
74.	$3C_2H_5Br \rightarrow C_2H_4 + 3HBr + C_2H_5 + C_2H_3$		
59 Goldberg, et. al. (1957)	T = 583 - 749 °K Pyrolysis reaction	A = 6.34 x 10^{11} s^{-1} E_a = 46400 ± 500 cal/mole	Added HBr enhances rate Added C_2H_4 inhibits rate

Table 1.- Continued

74. $3C_2H_5Br \rightarrow C_2H_4 + 3HBr + C_2H_5 + C_2H_3$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
59(continued)	Product analysis: titration of HBr		Mechanism: 1) $C_2H_5Br \rightarrow C_2H_4 + HBr$ 2) $C_2H_5Br_{wall} + HBr_{wall} \rightarrow C_2H_6 + Br_2$ 3) $M + Br_2 \rightarrow 2Br + M$ 4) $Br + C_2H_5Br \rightarrow C_2H_4Br + HBr$ 5) $C_2H_4Br \rightarrow C_2H_4 + Br$ 6) $Br + C_2H_4 \rightarrow C_2H_3 + HBr$ 7) $Br + C_2H_6 \rightarrow C_2H_5 + HBr$ Main products from step 5 Step 4 is slow and endothermic Steps 6 and 7 are relatively slow
75.	$C_2H_6 + F \rightarrow HF + C_2H_5$		
48 Fettis, et. al. (1964)	T = 165 - 351 °K F atoms from microwave discharge Product analysis: GC	Transition state theory: $A = 4.49 \times 10^{-11}$ cm^3/mol-s E_a = 220 cal/mole	
52 Foon, et. al. (1971)	Photolysis of F_2 to produce F atoms Product analysis: GC	E_a = 490 cal/mole $A = 1.0 \times 10^{-13}$ cm^3/mol-s (assumed) $k_{298\ °K} = 4.36 \times 10^{-12}$ cm^3/mol-s	
76.	$C_2H_6 + Br \rightarrow C_2H_5 + HBr$		
33 Coomber, et. al. (1966)	T = 293 °K Thermal reaction Product analysis: IR, VPC	E_a = 12.3 kcal/mole $A = 3.26 \times 10^{-11}$ cm^3/mol-s	

Table 1.- Continued

77.	$C_2H_5F + Br \rightarrow CH_3CHF + HBr$		
Ref.	Kinetic Methods	Rate Data	Comments
33 Coomber, et. al. (1966)	T = 293 °K Thermal reaction Product analysis: IR, VPC	E_a = 10.3 kcal/mole $A = 3.99 \times 10^{-12}$ cm^3/mol-s	
78.	$CH_3CHF_2 + Br \rightarrow CH_3CF_2 + HBr$		
33 Coomber, et. al. (1966)	T = 293 °K Thermal reaction Product analysis: IR, VPC	E_a = 13.3 kcal/mole $A = 5.5 \times 10^{-12}$ cm^3/mol-s	
79.	$CH_3CF_3 + Br \rightarrow CH_2CF_3 + HBr$		
33 Coomber, et. al. (1966)	T = 293 °K Thermal reaction Product analysis: IR, VPC	E_a = 22.2 kcal/mole $A = 2.5 \times 10^{-11}$ cm^3/mol-s	
80.	$CHF_2CHF_2 + Br \rightarrow CHF_2CF_2 + HBr$		
33 Coomber, et. al. (1966)	T = 293 °K Thermal reaction Product analysis: IR, VPC	E_a = 18.1 kcal/mole $A = 9.3 \times 10^{-12}$ cm^3/mol-s	
81.	$CF_3CH_2F + Br \rightarrow CF_3CHF + HBr$		
33 Coomber, et. al. (1966)	T = 293 °K Thermal reaction Product analysis: IR, VPC	E_a = 18.2 kcal/mole $A = 9.0 \times 10^{-12}$ cm^3/mol-s	

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
82.	$CF_3CHF_2 + Br \rightarrow CF_3CF_2 + HBr$		
143 Tarr, et. al. (1965)	Thermal reaction Product analysis: GC	$E_a = 18.0$ kcal/mole $A = 2.7 \times 10^{-12}$ cm^3/mol-s	
83.	$2CClF_2CClF_2 + F_2 \rightarrow 2CClF_2CF_3 + 2ClF$		
54 Foon, et. al. (1972)	$T = 732 - 798$ °K Static system Product analysis: GC	Rate = $k[F_2]^{1/2}[CClF_2CClF_2]$ $E_a = 36.450 \pm 0.300$ kcal/mole $A = (206 \pm 80)$ $cm^{3/2}/mol^{1/2}$-s	Mechanism for $R = CClF_2CF_2$: 1) $F_2 + M \rightarrow 2F + M$ 2) $F + RCl \rightarrow ClF + R$ 3) $R + ClF \rightarrow RCl + F$ 4) $R + F_2 \rightarrow RF + F$ 5) $R + ClF \rightarrow RF + Cl$ 6) $Cl + F_2 \rightarrow ClF + F$ 7) $F + F + M \rightarrow F_2 + M$
84.	$CF_3CClF_2 + F_2 \rightarrow C_2F_6 + ClF$		
54 Foon, et. al. (1972)	$T = 805.5$ °K Static system Product analysis: GC	Rate = $k[F_2]^{1/2}[C_2F_5Cl]$ $E_a = 36.520 \pm 0.300$ kcal/mole $A = (81.8 \pm 1.0)$ $cm^{3/2}/mol^{1/2}$-s	Mechanism is identical to the mechanism of reaction 83; $R = CF_3CF_2$
85.	$4CCl_3CHCl_2 + Cl_2 + 2\ O_2 \rightarrow C_2Cl_6 + 2CCl_3COCl + 2COCl_2 + 4HCl$		
105 Miller, et. al. (1956)	$T = 353 - 373$ °K Photolytic reaction Product analysis: derivative preparation and characterization		Mechanism: 1) $Cl_2 + h\nu \rightarrow 2Cl$ 2) $CCl_3CHCl_2 + Cl \rightarrow CCl_3CCl_2 + HCl$ 3) $CCl_3CCl_2 + Cl_2 \rightarrow CCl_3CCl_3 + Cl$ 4) $CCl_3CCl_2 + O_2 \rightarrow CCl_3CCl_2O_2$

85.	$4CCl_3CHCl_2 + Cl_2 + 2\ O_2 \rightarrow C_2Cl_6 + 2CCl_3COCl + 2COCl_2 + 4HCl$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
105(continued)			5) $CCl_3CCl_2O_2 \rightarrow CCl_3COCl + ClO$ 6) $CCl_3CCl_2O_2 \rightarrow 2COCl_2 + Cl$ 7) $CCl_3CHCl_2 + ClO \rightarrow CCl_3COCl + HCl + Cl$
86.	$CCl_3CHCl_2 + F_2 \rightarrow HF + CCl_3CCl_2F$		
105 Miller, et. al. (1956)	T = 370 - 378 °K Product analysis: titration, derivative preparation and characterization Thermal reaction		Mechanism: 1) $CCl_3CHCl_2 + F_2 \rightarrow CCl_3CCl_2 + HF + F$ 2) $CCl_3CCl_2 + F \rightarrow CCl_3CCl_2F$ 3) $CCl_3CHCl_2 + F \rightarrow CCl_3CCl_2 + HF$
87.	$F + CHF_3 \rightarrow HF + CF_3$		
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: GC, MS, IR	$k = 1.9 \times 10^{-13}\ cm^3/mol\text{-}s$	
88.	$F_2 + CHF_3 \rightarrow CF_4 + HF$		
31 Clyne, et. al. (1973)	T = 301 - 667 °K F atoms from microwave discharge Fast flow reactor Product anaylsis: MS	Pseudo-first order analysis $\Delta U^o_{298\ ^oK} = -33.7$ kcal/mole $A = 1.06 \pm 0.24 \times 10^{-11}\ cm^3/mol\text{-}s$ $E_a = 1040 \pm 326$ cal/mole	Mechanism: 1) $F + CHF_3 \rightarrow CF_3 + HF$ 2) $CF_3 + F_2 \rightarrow CF_4 + F$
89.	$CHF_3 + Br \rightarrow HBr + CF_3$		
143 Tarr, et. al. (1965)	Product analysis: GC	$E_a = 21.1$ kcal/mole $A = 3.15 \times 10^{-12}\ cm^3/mol\text{-}s$	

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
90.	$F + CHClF_2 \rightarrow HF + CClF_2$		
51 Foon, et. al. (1969)	F atoms from discharge Static system Product analysis: GC	$A = 4.7 \times 10^{-14}$ cm^3/mol-s $E_a = 1.2$ kcal/mole $k_{298\ ^{\circ}K} = 5.0 \times 10^{-13}$ cm^3/mol-s	
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: GC, MS, IR	$k_{298\ ^{\circ}K} = 2.3 \times 10^{-12}$ cm^3/mol-s	
91.	$F + CHCl_3 \rightarrow HF + CCl_3$		
31 Clyne, et. al. (1973)	F atoms from microwave discharge Fast flow reactor Product analysis: MS	$k_{300\ ^{\circ}K} = (5.3 \pm 1.3) \times 10^{-12}$ cm^3/mol-s $\Delta U^{o}_{298\ ^{\circ}K} = -45.55$ kcal/mole	
51 Foon, et. al. (1969)	F atoms from discharge Static system Product analysis: GC	$A = (3.1 \pm 0.2) \times 10^{-14}$ cm^3/mol-s $E_a = 657 \pm 48$ cal/mole $k_{298\ ^{\circ}K} = 1.0 \times 10^{-12}$ cm^3/mol-s	
92.	$F + CHCl_2F \rightarrow HF + CCl_2F$		
51 Foon, et. al. (1969)	F atoms from discharge Static system Product analysis: GC	$A = 1.06 \times 10^{-11}$ cm^3/mol-s $E_a = 1.29$ kcal/mole $k_{298\ ^{\circ}K} = 1.2 \times 10^{-12}$ cm^3/mol-s	
93.	$F + CH_2F_2 \rightarrow HF + CHF_2$		
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: MS, GC, IR	$k = 1.1 \times 10^{-11}$ cm^3/mol-s	

Table 1.– Continued

94.	$Br + CH_2F_2 \rightarrow HBr + CHF_2$		
Ref.	Kinetic Methods	Rate Data	Comments
143 Tarr, et. al. (1965)	Product analysis: GC	E_a = 15.3 kcal/mole A = 5.5 x 10^{-12} cm^3/mol-s	
95.	$F + CH_2Cl_2 \rightarrow HF + CHCl_2$		
31 Clyne, et. al. (1973)	F atoms from microwave discharge Fast flow reactor Product analysis: MS	$k_{300\ °K} \doteq (9.6 \pm 2.4) \times 10^{-12}$ cm^3/mol-s	
51 Foon, et. al. (1969)	F atoms from discharge Static system Product analysis: GC	A = 2.2 x 10^{-14} cm^3/mol-s E_a = 144 cal/mole $k_{298\ °K} = 3.4 \times 10^{-12}$ cm^3/mol-s	
96.	$F + CH_3F \rightarrow HF + CH_2F$		
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: MS, GC, IR	k = 8.8 x 10^{-11} cm^3/mol-s	
97.	$CH_3F + Br \rightarrow CH_2F + HBr$		
143 Tarr, et. al. (1965)	Product analysis: GC	E_a = 14.8 kcal/mole A = 1.2 x 10^{-11} cm^3/mol-s	
98.	$F + CH_3Cl \rightarrow HF + CH_2Cl$		
31 Clyne, et. al. (1973)	F atoms from microwave discharge Fast flow reactor Product analysis: MS	$k_{300\ °K} = (2.4 \pm 0.7) \times 10^{-11}$ cm^3/mol-s	

Table 1.- Continued

98.	$F + CH_3Cl \rightarrow HF + CH_2Cl$ (continued)		
Ref.	**Kinetic Methods**	**Rate Data**	**Comments**
51 Foon, et. al. (1969)	F atoms from discharge Static system Product analysis: GC	$A = 5.3 \times 10^{-11}$ cm^3/mol-s E_a = 1.01 kcal/mole	
52 Foon, et. al. (1971)	F atoms from discharge Static system Product analysis: GC	E_a = 1.08 kcal/mole $A = 1.27 \times 10^{-13}$ cm^3/mol-s $k_{298\,°K} = 2.0 \times 10^{-12}$ cm^3/mol-s	
99.	$6F_2 + 5CH_3I \rightarrow 2CH_2F_2 + 2CH_3F + I_2 + 3HF + CH_2IF + IF^* + IF$		
135 Rusin, et. al. (1967)	T = 298 °K Zone reactor Product analysis: EPR		Reaction accompanied by chemiluminescence in the UV and visible regions Mechanism: 1) $CH_3I + F \rightarrow CH_2I + HF$ 2) $CH_2I + F_2 \rightarrow CH_2IF^* + F$ 3) $CH_3I + F \rightarrow CH_3F + I$ 4) $CH_2IF^* + M \rightarrow CH_2IF + M$ 5) $CH_2IF^* \rightarrow CH_2F + I$ 6) $CH_2F + F_2 \rightarrow CH_2F_2 + F$ 7) $I + I + M \rightarrow I_2 + M$ 8) $I + F + M \rightarrow IF^* + M$ 9) $CH_2I + F \rightarrow CH_2 + IF$ 10) $CH_2 + F_2 \rightarrow CH_3F + F$
100.	$F + CH_4 \rightarrow HF + CH_3$		
3[illegible] Clyne, et. al. [illegible]	T = 300 °K F atoms from [illegible] discharge	$k_{300\,°K}$ = [illegible] E_a = [illegible] kcal/mole	[illegible]

Table 1.- Continued

100. $F + CH_4 \rightarrow HF + CH_3$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
31(continued)	Product analysis: MS Fast flow reactor	Collisional efficiency ≈ 0.1	
150 Wagner, et. al. (1971)	T = 253 - 353 °K F atoms from microwave discharge Fast flow reactor Product analysis: MS	$A = 5.5 \times 10^{-11}$ cm^3/mol-s E_a = 1150 cal/mole	Major chain termination reaction: $2CH_3 + M \rightarrow C_2H_6$
91 Kompa, et. al. (1972)	Flash photolysis	$k_{298\ °K} = 7.1 \times 10^{-11}$ cm^3/mol-s	
52 Foon, et. al. (1971)	F atoms from discharge Static system Product analysis: GC	$k_{298\ °K} = 1.1 \times 10^{-11}$ cm^3/mol-s E_a = 1.81 kcal/mole	
103 Mercer, et. al. (1959).	T = 298 - 423 °K Thermal reaction Product analysis: MS	$E_1 - E_a \simeq 0.5 \pm 0.2$ kcal/mole	Mechanism: 1) $F_2 \rightarrow 2F$ 2) $F + CH_4 \rightarrow HF + CH_3$ 3) $CH_3 + F_2 \rightarrow CH_3F + F$ Chain mechanism Surface reactions were important
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: MS, GC, IR	$k_{298\ °K} = 1 \times 10^{-12}$ cm^3/mol-s	

Table 1.- Continued

100. $F + CH_4 \rightarrow HF + CH_3$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
48 Fettis, et. al. (1964)	$T = 165 - 351\ ^{\circ}K$ F atoms from microwave discharge Product analysis: GC	Transition state theory: $A = 2.64 \times 10^{-11}\ cm^3/mol\text{-}s$ $E_a = 1.21$ kcal/mole $\Delta S_t^{\neq} = 2.31$ cal/mole-°K $\Delta S_r^{\neq} = 5.51$ cal/mol-°K $\Delta S_v^{\neq} = 4.8$ cal/mole-°K	
101.	$CH_4 + Br \rightarrow CH_3 + HBr$		
143 Tarr, et. al. (1965)	Product analysis: GC	$E_a = 17.3$ kcal/mole $A = 2.3 \times 10^{-11}\ cm^3/mol\text{-}s$	
102.	$3CCl_4 + 6H + 2H_2 \rightarrow 6HCl + CH_2Cl_2 + CHCl_3 + CHCl$		
28 Clark, et. al. (1966)	$T = 298\ ^{\circ}K$ Flow system Product analysis: GC	$\Delta H_2 = +14$ kcal/mole $\Delta H_5 = -65$ kcal/mole $\frac{k_6}{k_7} = 6.34$ $\frac{k_3[M]}{k_4} = 4.30$ $\Delta H_6 = -45$ kcal/mole	Mechanism: 1) $CCl_4 + H \rightarrow CCl_3 + HCl$ 2) $CCl_3 + H \rightarrow CHCl_3^*$ 3) $CHCl_3^* + M \rightarrow CHCl_3 + M$ 4) $CHCl_3^* \rightarrow CCl_2 + HCl$ 5) $CCl_2 + H_2 \rightarrow CH_2Cl_2^*$ 6) $CCl_2 + HCl \rightarrow CHCl_3^*$ 7) $CH_2Cl_2^* + M \rightarrow CH_2Cl_2 + M$ 8) $CH_2Cl_2^* \rightarrow CHCl + HCl$ M = Ar
135 Shilov, et. al. (1960)	$T = 783 - 865\ ^{\circ}K$ Flow system Product analysis: MS	$k = 2.6 \times 10^{11} \exp\left(-\frac{4700}{RT}\right)\ s^{-1}$	Rate constant for $CHCl_3 \rightarrow CCl_2 + HCl$

Table 1.- Continued

103.	$F + CCl_4 \rightarrow CCl_3 + ClF$		
Ref.	Kinetic Methods	Rate Data	Comments
29 Clark, et. al. (1964)	F atoms from discharge Flow system Product analysis: titration	$k_{298\,^{o}K} = 3.3 \times 10^{-12}\ cm^3/mol\text{-}s$	
74 Homann, et. al. (1971)	Flame study $T = 1500 - 1600\ ^{o}K$ $P = 77$ torr Product analysis: MS	$k_{298\,^{o}K} = 6.6 \times 10^{-14}\ cm^3/mol\text{-}s$	
90 Kolb, et. al. (1972)	$T = 298\ ^{o}K$ Discharge-flow system Product analysis: MS	$k_{298\,^{o}K} = 4.0 \times 10^{-16}\ cm^3/mol\text{-}s$	
104	$F_2 + CCl_4 \rightarrow CCl_3F + ClF$		
54 Foon, et. al. (1972)	$T = 399$ and $498\ ^{o}K$ Static system Product analysis: GC	rate = $k[F_2]^{1/2}[CCl_4]$ $A = 130\ cm^{3/2}/mol^{1/2}\text{-}s$ $E_a = 28.64 \pm 0.10$ kcal/mole	M = He Mechanism: 1) $F_2 + M \rightarrow 2F + M$ 2) $F + CCl_4 \rightleftarrows ClF + CCl_3$ 3) $CCl_3 + F_2 \rightarrow CCl_3F + F$ 4) $CCl_3 + ClF \rightarrow CCl_3F + Cl$ 5) $Cl + F_2 \rightarrow ClF + F$ 6) $F + F + M \rightarrow F_2 + M$

Table 1.– Continued

105.	$F_2 + CFCl_3 \rightarrow CF_2Cl_2 + ClF$		
Ref.	Kinetic Methods	Rate Data	Comments
54 Foon, et. al. (1972)	T = 589 – 733 °K Static system Thermal reaction Product analysis: GC	$A = 40.7 \pm 0.4\ cm^{3/2}/mol^{1/2}\text{-}s$ $E_a = 31.49 \pm 0.10$ kcal/mole	M = He Mechanism: 1) $F_2 + M \rightarrow 2F + M$ 2) $F + CFCl_3 \rightleftarrows ClF + CFCl_2$ 3) $CFCl_2 + F_2 \rightarrow CF_2Cl_2 + F$ 4) $CFCl_2 + ClF \rightarrow CF_2Cl_2 + Cl$ 5) $Cl + F_2 \rightarrow ClF + F$ 6) $F + F + M \rightarrow F_2 + M$
53 Foon, et. al. (1971)	T = 491 – 598 °K Static system Thermal reaction Product analysis: GC	rate = $k[F_2]^{1/2}[CFCl_3]$ $k = 2.4 \times 10^{-4}\ cm^{3/2}/mol^{1/2}\text{-}s$ Step $\Delta H^{\neq}$ (kcal/mole) 1 36.8 2 15.1 3 -52.5 4 -24.7 5 -0.2 6 -76.2 7 -23.7 8 -36.8	No rate inhibition by ClF or O_2 Mechanism: 1) $F_2 + M \rightarrow 2F + M$ 2) $F + CFCl_3 \rightleftarrows ClF + CFCl_2$ 3) $ClF + CFCl_2 \rightarrow CF_2 + Cl$ 4) $ClF + F + M \rightarrow ClF_2 + M$ 5) $ClF_2 + F_2 \rightarrow ClF_3 + F$ 6) $CCl_2 + F_2 \rightarrow CF_2Cl_2 + F$ (unbalanced) 7) $Cl + F_2 \rightarrow ClF + F$ 8) $F + F + M \rightarrow F_2 + M$
106.	$F_2 + CF_2Cl_2 \rightarrow CF_3Cl + ClF$		
54 Foon, et. al. (1972)	T = 596 – 747 °K Static system	rate = $k[F_2]^{1/2}[CF_2Cl_2]$ $A = 205.\ cm^{3/2}/mol^{1/2}\text{-}s$	M = He R = CF_2Cl

Table 1.- Continued

106.	$F_2 + CF_2Cl_2 \rightarrow CF_3Cl + ClF$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
54(continued)	Product analysis: GC	$E_a = 34.92 \pm 0.30$ kcal/mole	Mechanism: 1) $F_2 + M \rightarrow 2F + M$ 2) $F + RCl \rightleftarrows ClF + R$ 3) $R + F_2 \rightarrow RF + F$ 4) $R + ClF \rightarrow RF + Cl$ 5) $Cl + F_2 \rightarrow ClF + F$ 6) $F + F + M \rightarrow F_2 + M$
107.	$CF_3Cl + F_2 \rightarrow CF_4 + ClF$		
54 Foon, et. al. (1972)	T = 732 - 798 °K Static system Product analysis: GC	rate = $k[F_2]^{1/2}[CF_3Cl]$ $A = 8.18 \pm 0.02\ cm^{3/2}/mol^{1/2}\text{-}s$ $E_a = 39.02$ kcal/mole	M = He $R = CF_3$ Mechanism is identical to the mechanism of reaction 106.
108.	$CF_4 + M \rightarrow CF_3 + F + M$		
110 Modica, et. al. (1968)	T = 1700 - 3000 °K Shock tube Product detection: UV	$k = \frac{1.02 \times 10^{11}}{T^{4.64}} \exp\left(-\frac{122421}{RT}\right) cm^3/mol\text{-}s$	M = Ar
109.	$CF_3Br + F \rightarrow CF_4 + Br$		
17, 18, 19, 20 Bozzelli, et. al. (1973)	T = 188 - 373 °K F atoms from microwave discharge Fast flow system Product analysis: molecular beam MS	$\Delta H = -105$ kcal/mole for $F + CF_3BrF \rightarrow CF_4 + BrF$	Negative E_a Postulated intermediate: CF_3BrF Concentration of F atoms determined from titration with H_2. Accuracy = ±15%

Table 1.- Continued

110.	$CF_3Br + F \rightarrow BrF + CF_3$		
Ref.	Kinetic Methods	Rate Data	Comments
115 Pollack, et. al. (1973)	Fast flow reactor Product analysis: MS, GC, IR	$k = 4.0 \times 10^{-15}$ cm^3/mol-s	
111.	$CCl_3Br + F \rightarrow CFCl_3 + Br$		
17, 18, 19 Bozzelli, et. al. (1973)	F atoms from microwave discharge $P = 1$ torr Absolute concentration of F atoms determined by titration with H_2 Fast flow reactor Product analysis: molecular beam MS	$\Delta H = -54 \pm 8$ kcal/mole	Study of halogen displacement mechanism; abstraction mechanism predominates
112.	$CCl_3Br + F \rightarrow BrF + CCl_3$		
17, 18, 19 Bozzelli, et. al. (1973)	F atoms from microwave discharge $P = 1$ torr Absolute concentration of F atoms determined by titration with H_2 Fast flow reactor Product analysis: molecular beam MS	$E_a = 0$ $\Delta H = -3 \pm 4$ kcal/mole $k = (9.3 \pm 4.6) \times 10^{-11}$ cm^3/mol-s	Abstraction mechanism
113.	$CF_3I + F \rightarrow CF_4 + I$		
17, 18, 19 Bozzelli, et. al. (1973)	F atoms from microwave discharge $P = 1$ torr Fast flow reactor	$\Delta H = -69 \pm 8$ kcal/mole	Study of halogen displacement mechanism; abstraction mechanism predominates

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
113.	$CF_3I + F \rightarrow CF_4 + I$ (continued)		
17, 18, 19 (continued)	Absolute concentration of F atoms determined by titration with H_2 Product analysis: molecular beam MS		
114.	$CF_3I + F \rightarrow IF + CF_3$		
17, 18, 19 Bozzelli, et. al. (1973)	F atoms from microwave discharge P = 1 torr Fast flow reactor Absolute concentration of F atoms determined by titration with H_2 Product analysis: MS	$E_a = 0$ $k = (1.2 \pm 0.5) \times 10^{-10}$ cm^3/mol-s $\Delta H = -10 \pm 5$ kcal/mole	Abstraction mechanism
1 Albright, et. al. (1969)	Product analysis: MS	$k = (1.66 \pm 0.66) \times 10^{-10}$ cm^3/mol-s	O_2 present
115.	$CF_3 + M \rightarrow CF_2 + F + M$		
110 Modica, et. al. (1968)	T = 1700 - 3000 °K Shock tube Product analysis: UV	$A = \frac{2.6 \times 10^{25}}{T^{9.04}}$ cm^3/mol-s E_a = 92254 cal/mole	
116.	$CF_3 + CF_3 + M \rightarrow C_2F_6 + M$		
110 Modica, et. al. (1968)	T = 1700 - 3000 °K Shock tube Product analysis: UV	$k = \frac{2.0 \times 10^{-30}}{T^{1/2}}$ cm^6/mol^2-s	M = Ar

Table 1.- Continued

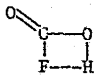
Ref.	Kinetic Methods	Rate Data	Comments
117.	$2CH_3 \rightarrow C_2H_6$		
13 Basco, et. al. (1970)	Flash photolysis Product analysis: optical absorption, VPC	$k = 4.32 \times 10^{-11}$ cm^3/mol-s	
118.	$CF_3 + F + M \rightarrow CF_4 + M$		
110 Modica, et. al. (1968)	T = 1700 - 3000 °K Shock tube Product analysis: UV	$A = \frac{2.67 \times 10^{-16}}{T^{4.64}}$ cm^6/mol^2-s E_a = 2849 cal/mole	M = Ar
119.	$CHFCl_2 + O_2 \rightarrow CO_2 + HF + 2Cl$		
60 Gordon, et. al. (1973)	T = 297 ± 2 °K Flash photolysis at $\lambda \geqq 1650$ A	$\Delta H_3 \approx -180$ kcal/mole	HF laser emissions: 15 observed from $\Delta v = 3 \rightarrow 2$ to $\Delta v = 1 \rightarrow 0$. Intensity increases linearly with flash energy. Only partial population inversion (typical of elimination reactions): $N_2/N_1 \approx 0.8$ Emissions due to steps 3 and 4 in mechanism. Mechanism: 1) $CHFCl_2 + h\nu \rightarrow CHFCl + Cl$ 2) $CHFCl + h\nu \rightarrow CHF + Cl$ 3) $CHF + O_2 \rightleftarrows CHFOO \rightarrow FCOOH^{\dagger}$ 4) $FCOOH^{\dagger} \rightarrow$  $\rightarrow HF + CO_2$

Table 1.– Continued

120.	$CH_3 + NO \rightarrow CH_3NO$		
Ref.	Kinetic Methods	Rate Data	Comments
13 Basco, et. al. (1970)	Flash photolysis Product analysis: optical absorption, VPC	$k = 4.0 \times 10^{-12}$ cm^3/mol-s	
121.	$CH_3 + NO_2 \rightarrow CH_3NO_2$		
68 Heicklen, et. al. (1968)		$k = 5.0 \times 10^{-12}$ cm^3/mol-s	
122.	$CH_3NO + CH_3 \rightarrow (CH_3)_2NO$		
68 Heicklen, et. al. (1968)		$k > 6.6 \times 10^{-14}$ cm^3/mol-s	
123.	$2CHF_2Cl \rightarrow 2HCl + C_2F_4$		
44, 45 Edwards, et. al. (1964, 1965)	Thermal reaction T = 806 – 1023 °K Flow and static systems Product analysis: GC	Derived at T = 298 °K: $\Delta H_f(CHF_2Cl) = -112.3$ kcal/mole $\Delta H_f(CF_2) = -39.1 \pm 6.0$ kcal/mole $k_1 = 6.9 \times 10^{13} \exp\left(-\frac{55790}{RT}\right) s^{-1}$ $k_2 = 0.354$ cm^3/mol-s $A_{-1} = 9.0 \times 10^{-13}$ cm^3/mol-s $E_{a,-1} = 6210$ cal/mole $k_{-2} = 4.6 \times 10^{16} \exp\left(-\frac{70360}{RT}\right) s^{-1}$ $E_{a,2} = 0$ (assumed)	Mechanism: 1) $CHF_2Cl \rightleftarrows CF_2 + HCl$ 2) $2CF_2 \rightleftarrows C_2F_4$ Side reactions: 3) $CF_2 + C_2F_4 \rightleftarrows CF_2CFCF_3$ 4) $C_2F_4 + HCl \rightleftarrows CHF_2CF_2Cl$ 5) $2C_2F_4 \rightleftarrows C_4F_8$ 6) $CHF_2Cl + C_2F_4 \rightleftarrows CHF_2CF_2CF_2Cl$ High A in k_{-2} explained by increased freedom of rotation in going from C_2F_4 to the transition state

Table 1.- Continued

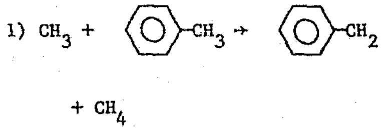
123.	$2CHF_2Cl \rightarrow 2HCl + C_2F_4$ (continued)		
Ref.	**Kinetic Methods**	**Rate Data**	**Comments**
12 Barnes, et. al. (1971)	Thermal reaction T = 727 - 796 °K Pyrolysis in static system Product analysis: gas burette	$A_1 = (4.0 \pm 2.8) \times 10^{12}\ s^{-1}$ $E_{a,1} = 52800 \pm 1500$ cal/mole $A_{-1} = (3.5 \pm 10.4) \times 10^{-13}\ cm^3/mol\text{-}s$ $E_{a,-1} = 12120 \pm 2700$ cal/mole $\Delta H_f^o (CF_2) = -49.5$ kcal/mole $\Delta S^o (CF_2) = 62.4$ cal/mole-°K	HCl inhibits rate Mechanism: 1) $CHF_2Cl \rightleftarrows CF_2 + HCl$ 2) $CF_2 + CF_2 \rightleftarrows C_2F_4$
124.	$CF_3 + CF_3 \rightarrow C_2F_6$		
4 Arthur, et. al. (1966)	λ > 3000 Å Vacuum system Product analysis: GC	$k = 3.8 \times 10^{-11}\ cm^3/mol\text{-}s$	
125.	$CH_3 + CH_3F \rightarrow CH_4 + CH_2F$		
118 Pritchard, et. al. (1965)		$E_a = 8.7 \pm 0.7$ kcal/mole Steric factor = 10^{-3}	Absolute activation energy obtained from competition reaction: $CD_3 + CD_3COCD_3 \rightarrow CD_4 + CD_2COCD_3$ Reproducible activation energy only at T > 473 °K
126.	$CH_3Br + CH_3 \rightarrow CH_3 + CH_3Br$		
46 Evans, et. al. (1960)	T = 388 °K Product analysis: radioactive labelling	$E_a - E_{a,1} = 1.8 \pm 1.5$ kcal/mole $\frac{A}{A_1} = 3$	Rate measured relative to: 1) 

Table 1.- Continued

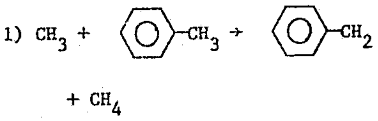
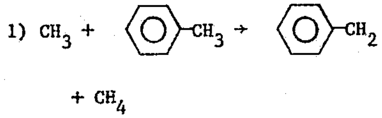
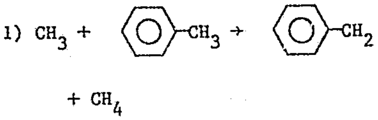
Ref.	Kinetic Methods	Rate Data	Comments
127.	$CH_3I + CH_3 \rightarrow CH_3 + CH_3I$		
46 Evans, et. al. (1960)	T = 338 °K Product analysis: radioactive labelling	$\frac{k}{k_1} = 45$	Rate measured relative to: 
128.	$CH_3 + CH_2F_2 \rightarrow CH_4 + CHF_2$		
118 Pritchard, et. al. (1965)		E_a = 10.2 ± 0.2 kcal/mole Steric factor = 10^{-3}	Absolute activation energy obtained from competition reaction: $CD_3 + CD_3COCD_3 \rightarrow CD_4 + CD_2COCD_3$
129.	$CH_2ClBr + CH_3 \rightarrow CH_3Br + CH_2Cl$		
46 Evans. et. al. (1960)	T = 338 °K Product analysis: radioactive labelling	$\frac{k}{k_1} = 6400$	Rate measured relative to: 
130.	$CH_2ClI + CH_3 \rightarrow CH_3I + CH_2Cl$		
46 Evans, et. al. (1960)	T = 338 °K Product analysis: radioactive labelling	$\frac{k}{k_1} = 6400$	Rate measured relative to: 
131.	$CF_2Br_2 + CH_3 \rightarrow CH_3Br + CF_2Br$		
145 Tomkinson, et. al. (1964)	T = 363 - 418 °K, λ= 2537 Å Product analysis: MS	E_a = 6.4 ± 1.0 kcal/mole A = 1.7×10^{-13} cm^3/mol-s	

Table 1.- Continued

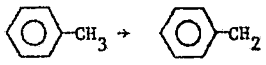
Ref.	Kinetic Methods	Rate Data	Comments
132.	$CH_3 + CHF_3 \rightarrow CH_4 + CF_3$		
117 Pritchard, et. al. (1964)		$E_a = 10.2 \pm 0.2$ kcal/mole $D(CF_3{-}H) = 105$ kcal/mole	
133.	$3CHCl_3 \rightarrow CCl_4 + 3HCl + CCl_2{=}CCl_2$		
133 Semeluk, et. al. (1957)	$T = 450 - 525$ °K Thermal reaction Static and flow systems Product analysis: pressure measurements	$E_a = 37.2 \pm 2.0$ kcal/mole $A = 6.3 \times 10^8\ s^{-1}$ $D(CHCl_2{-}Cl) \leq 72$ kcal/mole	Mechanism: 1) $CHCl_3 \rightarrow CHCl_2 + Cl$ 2) $Cl + CHCl_3 \rightleftarrows HCl + CCl_3$ 3) $CCl_3 + Cl \rightarrow CCl_4$ 4) $CCl_3 \rightarrow CCl_2 + Cl$ 5) $CCl_2 + CHCl_3 \rightarrow CCl_2{=}CCl_2 + HCl$
134.	$CHCl_2Br + CH_3 \rightarrow CH_3Br + CHCl_2$		
46 Evans, et. al. (1960)	$T = 338$ °K Product analysis: radioactive labelling	$\frac{k}{k_1} = 131$	Rate measured relative to: 1) CH_3 +  + CH_4
135.	$CBr_4 + CH_3 \rightarrow CH_3Br + CBr_3$		
145 Tomkinson, et. al. (1964)	$T = 363 - 418$ °K Product analysis: VPC	$E_a = 7.9 \pm 1.1$ kcal/mole $A = 2.64 \times 10^{-10}\ cm^3/mol\text{-}s$	

Table 1.- Continued

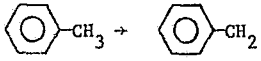
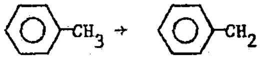
Ref.	Kinetic Methods	Rate Data	Comments
136.	$CCl_4 + CH_3 \rightarrow CH_3Cl + CCl_3$		
145 Tomkinson, et. al. (1964)	T = 363 - 413 °K λ = 2537 Å Product analysis: VPC	E_a = 12.9 ± 0.7 kcal/mole $A = 4.21 \times 10^{-11}$ cm^3/mol-s	
137.	$CCl_3Br + CH_3 \rightarrow CH_3Br + CCl_3$		
46 Evans, et. al. (1960)	T = 338 °K Product analysis: radioactive labelling	$\frac{k}{k_1} = 7400$	Rate measured relative to: 1) CH_3 +  + CH_4
138.	$CF_3I + CH_3 \rightarrow CH_3I + CF_3$		
46 Evans, et. al. (1960)	T = 338 °K Product analysis: radioactive labelling	$\frac{k}{k_1} = 20000$	Rate measured relative to: 1) CH_3 +  + CH_4
145 Tomkinson, et. al. (1964)	T = 363 - 413 °K λ = 2537 Å Product analysis: VPC	E_a = 7.5 ± 1.0 kcal/mole $A = 1.05 \times 10^{-10}$ cm^3/mol-s	
139.	$CF_3 + CH_3Br \rightarrow CF_3Br + CH_3$		
2 Alcock, et. al. (1965)		See reaction 55	

Table 1.- Continued

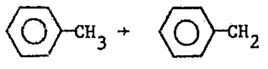
139.	$CF_3 + CH_3Br \rightarrow CF_3Br + CH_3$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
145 Tomkinson, et. al. (1964)	Reverse reaction studied T = 363 - 418 °K Product analysis: VPC	$E_a = 12.5 \pm 1.0$ kcal/mole $A = 3.34 \times 10^{-11}$ cm^3/mol-s	
140.	$C_2H_5I + CH_3 \rightarrow CH_3I + C_2H_5$		
46 Evans, et. al. (1960)	T = 338 °K Product analysis: radioactive labelling	$\frac{k}{k_1} = 180$ $E_a - E_{a,1} = -1.9 \pm 1.0$ kcal/mole $\frac{A}{A_1} = 10$	Rate measured relative to: 1) CH_3 +  + CH_4
141.	$CH_2CO \rightarrow CH_2 + CO$		
155 Wilson, et. al. (1958)	$\lambda = 2700 - 3100$ Å Product analysis: MS	$\frac{k_1}{k_2} = 2.7$ $\frac{k_3}{k_4} = 10.5$ $\frac{k_5}{k_4} = 0.8$ for $M = CH_2CO, SF_6$ $\frac{k_5}{k_4} = 0.1$ for $M = N_2$	$^3CH_2$ formed Mechanism: $CH_2CO + h\nu \rightarrow CH_2 + CO$ 1) $CH_2 + CH_2CO \rightarrow C_2H_4 + CO$ 2) $CH_2 + CO \rightarrow CH_2CO^*$ 3) $CH_2CO^* \rightarrow CH_2 + CO$ 4) $CH_2CO^* + CH_2CO \rightarrow 2CH_2CO$ 5) $CH_2CO^* + M \rightarrow CH_2CO + M$
38 DeGraff, et. al. (1967)	Reverse reaction studied T = 293 - 353 °K $\lambda = 2900 - 3340$ Å Product analysis: VPC, UV	$\frac{k_4}{k_3} = 3.6$ at $\lambda = 3160$ Å (λ dependent) $\frac{k_2}{k_1} = 0.14 \pm 0.2$ at $\lambda = 2900 - 3340$ Å	$^3CH_2$ more reactive than $^1CH_2$ with CO $^1CH_2$ more reactive than $^3CH_2$ with CH_2CO Mechanism: 1) $^1CH_2 + CH_2CO \rightarrow$ products

Table 1.- Continued

141. $CH_2CO \rightarrow CH_2 + CO$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
38(continued)		$\frac{k_5}{k_1} = 0.01$ for $M = N_2$, CO For $CH_2CO + h\nu \rightarrow {}^1CH_2 + CO$, quantum yield of ${}^1CH_2 = 0.53 \pm 0.03$	2) ${}^1CH_2 + CO \rightarrow CH_2CO$ 3) ${}^3CH_2 + CH_2CO \rightarrow$ products 4) ${}^3CH_2 + CO \rightarrow CH_2CO$ 5) ${}^1CH_2 + M \rightarrow {}^3CH_2 + M$ $M = N_2$, CO O_2 selectively removes ${}^3CH_2$
34 Dalby, (1964)	λ = 2537 Å Hg sensitized decomposition Product analysis: GC		${}^3CH_2$ is predominate product
5 Avery, et. al. (1968)	T = 298 ± 2 °K λ = 2537 Å Hg sensitized decomposition Product analysis: GC, pressure measurements	Quantum yields (Φ): At $P_{CH_2CO} = 10$ torr, $\Phi_{CO} = 1.0$ mol/photon At $P_{CH_2CO} = 365$ torr, $\Phi_{CO} = 1.51$ mol/photon	${}^3CH_2$ is predominate product Mechanism: 1) $Hg({}^1S_o) + h\nu \rightarrow Hg({}^3P_1)$ 2) $Hg({}^3P_1) + CH_2CO \rightarrow Hg({}^1S_o) + {}^3(CH_2CO)$ 3) ${}^3(CH_2CO) \rightarrow {}^3CH_2 + CO$ 4) ${}^3CH_2 + C_2H_4 \rightarrow {}^\cdot CH_2CH_2CH_2{}^{*\cdot}$ 5) ${}^3CH_2CH_2CH_2{}^* \rightarrow H + CH_2CHCH_2$ 6) ${}^3CH_2CH_2CH_2{}^* \rightarrow \nabla^*$ 7) ${}^3CH_2CH_2CH_2{}^* \rightarrow CH_3CH{=}CH_2{}^*$ 8) $\nabla^* \rightarrow CH_3CH{=}CH_2{}^*$ 9) $\nabla^* + M \rightarrow \nabla + M$ 10) $CH_3CH{=}CH_2{}^* \rightarrow H + CH_2CHCH_2$ 11) $CH_3CH{=}CH_2{}^* + M \rightarrow CH_3CH{=}CH_2 + M$ 12) $H + CH_2CO \rightarrow CH_3 + CO$ 13) $H + C_2H_4 \rightarrow C_2H_5$

Table 1.- Continued

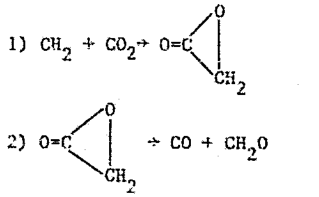
Ref.	Kinetic Methods	Rate Data	Comments
141.	$CH_2CO \rightarrow CH_2 + CO$ (continued)		
5(continued)			14) $CH_3 + CH_3 \rightarrow C_2H_6$ 15) $CH_3 + C_2H_5 \rightarrow C_3H_8$ 16) $C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}$ 17) $C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4$ 18) $CH_3 + CH_2=CHCH_2 \rightarrow CH_3CH_2CH=CH_2$ 19) $^3CH_2 + CH_2CO \rightarrow CH_3 + CHCO$
63 Halberstadt, et. al. (1967)	λ = 3130 Å Product analysis: GC	RRKM theory $D(CH_2\text{—}CO)$ = 81.9 kcal/mole at 298 °K $E(^1CH_2) = E(^3CH_2)$ + 2.5 kcal/mole	
89 Kistiakowsky, et. al. (1958)	Two wavelength regions: $\lambda_I > 2300$ Å $\lambda_{II} > 2900$ Å Product analysis: GC, MS	Quantum yield of CO not changed by increasing the intensity of radiation $\frac{\text{Rate } (CH_2 + CO_2)}{\text{Rate } (CH_2 + CH_2CO)} = 2 \times 10^{-2}$	Not an association mechanism Mechanism for $CH_2 + CO_2 \rightarrow CO + CH_2O$:  1) $CH_2 + CO_2 \rightarrow$ 2) $\rightarrow CO + CH_2O$
142.	$CH_2N_2 \rightarrow {}^1CH_2 + N_2$		
136 Shilov, et. al. (1968)	T = 300 °K Product analysis: IR, MS	RRKM theory For step 2, E_a = 8 kcal/mole For step 5, E_a = 16 kcal/mole	Only CF_3CH and NCCH react with N_2 Mechanism: 1) $CH_2N_2 + M \rightarrow {}^1CH_2 + N_2 + M$ 2) $^1CH_2 + N_2 + M \rightarrow CH_2N_2 + M$ 3) $^1CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2$ 4) $^1CH_2 + M \rightarrow {}^3CH_2 + M$

Table 1.- Continued

142.	$CH_2N_2 \rightarrow {}^1CH_2 + N_2$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
136(continued)			5) ${}^3CH_2 + N_2 + M \rightarrow CH_2N_2 + M$ 6) ${}^3CH_2 + {}^3CH_2 + M \rightarrow C_2H_4 + M$
143.	$CF_2 + M \rightarrow CF + F + M$		
107 Modica, et. al. (1966)	T = 2600 - 3700 °K Shock tube P ≃ 325 torr Product analysis: absorption at 2536 Å	$A = \frac{6.98 \times 10^2}{T^{2.85}}$ cm^3/mol-s E_a = 106000 cal/mole	
144.	$5CH_4 \rightarrow {}^3CH_2 + 2CH_3 + 3H_2 + C_2H_6$		
122 Rebbert, et. al. (1971)	λ = 1048 - 1067 Å, 1236 Å P = 5 - 2200 torr	Quantum yields (Φ): At 1236 Å, $\Phi_{C_2H_6}$ = 0.32 ± 0.03 mol/photon At 1048 - 1067 Å, $\Phi_{C_2H_6}$ = 0.29 ± 0.04 mol/photon $\frac{k_2}{k_5} = 0.67$	Mechanism: 1) $CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$ 2) ${}^1CH_2 + CH_4 \rightarrow C_2H_6^*$ 3) $C_2H_6^* + M \rightarrow C_2H_6 + M$ 4) $C_2H_6^* \rightarrow 2CH_3$ 5) ${}^1CH_2 + CH_4 \rightarrow {}^3CH_2 + CH_4$
21 Braun, et. al. (1970)	Flash photolysis T = 298 °K P = 25 - 300 torr Product analysis: UV	Using above mechanism: $k_2 = 1.9 \pm 0.5 \times 10^{-12}$ cm^3/mol-s $k_5 = 1.6 \pm 0.5 \times 10^{-12}$ cm^3/mol-s	Four experimental points
145.	$CF_2 + CFCl \rightarrow CF_2CFCl$		
147 Tyerman, et. al. (1969)	T = 298 °K λ = 2490 Å	$k \simeq (1 \pm 0.8) \times 10^{-12}$ cm^3/mol-s	

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
145.	$CF_2 + CFCl \rightarrow CF_2CFCl$ (continued)		
147(continued)	Flash photolysis Product analysis: UV		
146.	$2CF_2 \rightarrow C_2F_4$		
36 Dalby, et. al. (1964)	$T = 298 - 572\ ^{o}K$ Flash photolysis Product analysis: UV	$E_a = 1.2$ kcal/mole $k_{298\ ^{o}K} = (1.41 \pm 1.06) \times 10^{-14}$ cm^3/mol-s	O_2 has no effect on rate
147 Tyerman, et. al. (1969)	$T = 298\ ^{o}K$ Flash photolysis $\lambda = 2490$ Å Product analysis: UV	$A = \dfrac{(4.15 \pm 0.83) \times 10^{-15}}{T^{1/2}}$ cm^3/mol-s $E_a = 400 \pm 100$ cal/mole	Added C_2H_4 has no effect on rate
159 Zmbov, et. al. (1968)	Shock tube $T = 1127 - 1244\ ^{o}K$ Product analysis: MS	$D(CF_2{=}CF_2) = 76.3 \pm 3$ kcal/mole	
108 Modica, et. al. (1967)	$T = 1200 - 1600\ ^{o}K$ Shock tube Product analysis: UV	$A = \dfrac{(5.66 \pm 1.29) \times 10^{-10}}{T^{(6.36 \pm 0.55)}}$ cm^6/mol^2-s $E_a = 1840 \pm 263$ cal/mole $A_r = \dfrac{(6.78 \pm 1.20) \times 10^{16}}{T^{(6.36 \pm 0.55)}}$ cm^3/mol-s $E_{a,\ r} = 74900 \pm 3000$ cal/mole $D(CF_2{-}CF_2) = 74.9$ kcal/mole	N_2 is inert gas r = reverse reaction
26 Carlson, et. al. (1971)	$T = 1240 - 1600\ ^{o}K$ Shock tube	$\Delta H_r = 68.4 \pm 0.8$ kcal/mole $\Delta H_f(CF_2) = -44.5 \pm 0.4$ kcal/mole	r = reverse reaction

Table 1.- Continued

Ref.	Kinetic Methods	Rate Data	Comments
146.	$2CF_2 \rightarrow C_2F_4$ (continued)		
26(continued)	λ = 2200 - 2900 Å Product analysis: UV	$\Delta H_f(C_2F_4)$ = -157.4 kcal/mole $E_{a,r}$ = 54300 ± 260 cal/mole $A_r = (8.9 \pm 1.8) \times 10^2$ $cm^{3/2}/mol^{1/2}$-s	
147.	$3H + 7CH_2N_2 + H_2 \rightarrow C_2H_4 + 2CH_4 + CHN_2 + C_2H_6 + 6N_2$		
14 Bell, et. al. (1962)	T = 195 °K Photolytic excitation by Hg arc		Mechanism: 1) $CH_2N_2 + h\nu \rightarrow CH_2 + N_2$ 2) $CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2$ 3) $CH_2 + H_2 \rightarrow CH_4{}^*$ 4) $M + CH_4{}^* \rightarrow CH_4 + M$ 5) $H + CH_2N_2 \rightarrow CH_3 + N_2$ 6) $CH_3 + CH_2N_2 \rightarrow CH_3CH_2N_2$ 7) $CH_3 + CH_3 \rightarrow C_2H_6$ 8) $CH_3CH_2N_2 \rightarrow CH_4 + CHN_2$
148.	$CF_2 + F + M \rightarrow CF_3 + M$		
110. Modica, et. al. (1968)	T = 1700 - 3000 °K Shock tube Product analysis: UV at λ = 2660 Å	$A = \frac{4.12 \times 10^{-2}}{T^{9.04}}$ cm^6/mol^2-s E_a = 2287 cal/mole	
149	$5CH_2CO + 4H_2 \rightarrow C_2H_6 + 5CO + C_2H_4 + CH_4 + 4H$		
116 Powell- Wiffen, et. al. (1968)	λ = 2500 - 3400 Å T = 298 °K Product analysis: GC	$k_4k_3{}^{1/2} = 2.8 \times 10^{-15}$ $cm^{3/2}/mol^{1/2}$-s	CO used to scavenge $^3CH_2$ Mechanism: 1) $CH_2CO + h\nu \rightarrow CH_2 + CO$ 2) $CH_2 + H_2 \rightarrow CH_3 + H$

Table 1.- Continued

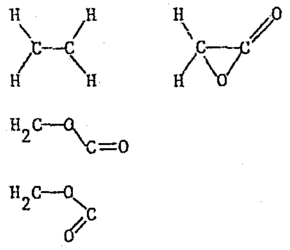
149.	$5CH_2CO + 4H_2 \rightarrow C_2H_6 + 5CO + C_2H_4 + CH_4 + 4H$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
116(continued)			3) $2CH_3 \rightarrow C_2H_6$ 4) $CH_3 + H_2 \rightarrow CH_4 + H$ 5) $CH_2 + CH_2CO \rightarrow C_2H_4 + CO$
150.	$^1CH_2 + CH_4 \rightarrow C_2H_6$		
62 Halberstadt, et. al. (1973)	$\lambda = 3130$ Å Product analysis: GC	$k = 1.9 \times 10^{-12}$ $cm^3/mol\text{-}s$ $^1CH_2 = {}^3CH_2 + 2.5$ kcal/mole	Insertion reaction
151.	$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2$		
21 Braun, et. al. (1970)	Flash photolysis of CH_2CO to produce $^3CH_2$ T = 298 °K Product analysis: UV at 1415 Å	$k = (5.3 \pm 1.5) \times 10^{-11}$ $cm^3/mol\text{-}s$	
152.	$^1CH_2 + H_2 \rightarrow CH_3 + H$		
21 Braun, et. al. (1970)	Flash photolysis of CH_2N_2 and CH_2CO to produce $^1CH_2$ T = 298 °K Product analysis: UV at 1415 Å	$k = (7.0 \pm 1.5) \times 10^{-12}$ $cm^3/mol\text{-}s$	Mechanism: 1) $^1CH_2 + H_2 \rightarrow CH_4^*$ 2) $CH_4^* \rightarrow CH_3 + H$
153.	$^1CH_2 + H_2 \rightarrow {}^3CH_2 + H_2$		
21 Braun, et. al. (1970)	Flash photolysis of CH_2N_2 and CH_2CO to yield $^1CH_2$ T = 298 °K Product analysis: UV at 1415 Å	$k < 1.5 \times 10^{-12}$ $cm^3/mol\text{-}s$	

Table 1.- Continued

154.	${}^1CH_2 + M \rightarrow {}^3CH_2 + M$		
Ref.	Kinetic Methods	Rate Data	Comments
21 Braun, et. al. (1970)	Flash photolysis of CH_2N_2 and and CH_2CO to produce ${}^1CH_2$ T = 298 °K Product analysis: UV at 1415 Å	For M = He: $k = (3.0 \pm 0.7) \times 10^{-13}$ $cm^3/mol\text{-}s$ For M = Ar: $k = (6.7 \pm 1.3) \times 10^{-13}$ $cm^3/mol\text{-}s$ For $M = N_2$: $k = (9.0 \pm 2.0) \times 10^{-13}$ $cm^3/mol\text{-}s$	
155.	${}^3CH_2 + H_2 \rightarrow CH_3 + H$		
21 Braun, et. al. (1970)	Flash photolysis of CH_2CO to produce ${}^3CH_2$ T = 298 °K Product analysis: UV	$k < 5 \times 10^{-14}$ $cm^3/mol\text{-}s$	
156.	${}^3CH_2 + CH_4 \rightarrow 2CH_3$		
21 Braun, et. al. (1970)	Flash photolysis of CH_2CO to produce ${}^3CH_2$ T = 298 °K Product analysis: UV	$k < 5 \times 10^{-14}$ $cm^3/mol\text{-}s$	
157.	$4CH_2N_2 + 2CH_4 \rightarrow C_2H_4 + 2C_2H_6 + 4N_2$		
14 Bell, et. al. (1962)	T = 195 °K Excitation by Hg arc Product analysis: MS, GC		Mechanism: 1) $CH_2N_2 + h\nu \rightarrow CH_2 + N_2$ 2) $CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2$ 3) $CH_2 + CH_4 \rightarrow C_2H_6^*$ 4) $C_2H_6^* + M \rightarrow C_2H_6 + M$ 5) $C_2H_6^* \rightarrow 2CH_3$ 6) $2CH_3 \rightarrow C_2H_6$

Table 1.– Continued

158. $CH_2N_2 + CO_2 \rightarrow H_2CO + CO + N_2$

Ref.	Kinetic Methods	Rate Data	Comments
106 Milligan, et. al. (1962)	T = 53 °K $\lambda > 1900$ Å Product analysis: IR		Postulated intermediates in the reaction:  Spectral assignments

159. $9CH_2CO + 9CH_3Cl \rightarrow 9CO + 2C_2H_4 + 2HCl + 2C_2H_6 + CH_4 + CH_2Cl_2 + 2C_2H_5Cl + C_2H_4Cl_2 + C_2H_3Cl$

Ref.	Kinetic Methods	Rate Data	Comments
83 Johnstone, et. al. (1967)	$\lambda_I = 2600 - 3200$ Å $\lambda_{II} = 3200 - 3800$ Å	$k_3 \approx k_4 \approx k_7$ $\left(\frac{k_6}{k_5}\right)_I = 1.3 \times 10^{-2}$ mole/l $\left(\frac{k_6}{k_5}\right)_{II} = 2.1 \times 10^{-2}$ mole/l $(k_2\ I_o)_I = 1.7 \times 10^{-6}\ s^{-1}$ $(k_2\ I_o)_{II} = 8.8 \times 10^{-6}\ s^{-1}$	Recombination processes are exothermic Abstraction mechanism: 1) $CH_2 + CH_3Cl \rightarrow CH_2Cl + CH_3$ 2) $CH_2CO + h\nu \rightarrow CH_2 + CO$ 3) $CH_2Cl + CH_3 \rightarrow C_2H_5Cl^*$ 4) $2CH_3 \rightarrow C_2H_6$ 5) $C_2H_5Cl^* + M \rightarrow C_2H_5Cl + M$ 6) $C_2H_5Cl^* \rightarrow C_2H_4 + HCl$ 7) $2CH_2Cl \rightarrow C_2H_4Cl_2^*$ 8) $C_2H_4Cl_2^* + M \rightarrow C_2H_4Cl_2 + M$ 9) $C_2H_4Cl_2^* \rightarrow C_2H_3Cl + HCl$ 10) $CH_2Cl + CH_3Cl \rightarrow CH_2Cl_2 + CH_3$ 11) $CH_3 + CH_3Cl \rightarrow CH_4 + CH_2Cl$ 12) $CH_2 + CH_2CO \rightarrow C_2H_4 + CO$

Table 1.- Continued

159. $9CH_2CO + 9CH_3Cl \rightarrow 9CO + 2C_2H_4 + 2HCl + 2C_2H_6 + CH_4 + CH_2Cl_2 + 2C_2H_5Cl + C_2H_4Cl_2 + C_2H_3Cl$ (continued)

Ref.	Kinetic Methods	Rate Data	Comments
134 Setser, et. al. (1965)	P = 10 - 1500 torr λ = 3200 Å Product analysis: GC	Steps 1, 3, 4, 7, and 8 are exothermic by 80 - 85 kcal/mole	Cl abstraction predominates; less than 5% insertion occurs. Using the mechanism above(ref. 83) steps 1 - 8 are important
11 Bamford, et. al. (1965)	λ = 2450 - 4000 Å Product analysis: VPC		Major products: C_2H_6, CH_2Cl_2 CH_2 is six times more reactive with CH_2CO than with CH_3Cl
82 Johnstone, et. al. (1966)	Photolysis of CH_2CO to produce CH_2 λ_1 = 2500 - 3400 Å λ_2 = 3000 - 3800 Å Product analysis: VPC	Relative rate of formation of C_2H_6 to C_2H_5Cl is pressure dependent If $[CH_3] \approx [CH_2Cl]$, $k_4 = 2k_5$	Mechanism: 1) $CH_2CO + h\nu \rightarrow CH_2 + CO$ 2) $CH_2 + CH_2CO \rightarrow C_2H_4 + CO$ 3) $CH_2 + CH_3Cl \rightarrow CH_2Cl + CH_3$ 4) $2CH_3 \rightarrow C_2H_6$ 5) $CH_3 + CH_2Cl \rightarrow C_2H_5Cl^*$ 6) $C_2H_5Cl^* + M \rightarrow C_2H_5Cl + M$ 7) $C_2H_5Cl^* \rightarrow C_2H_4 + HCl$

160.

$$^1CH_2 + CH_2F_2 \xrightarrow{a} C_2H_3F + HF$$

$$^1CH_2 + CH_2F_2 \xrightarrow{i} C_2H_4F_2$$

Ref.	Kinetic Methods	Rate Data	Comments
119 Pritchard, et. al. (1965)	λ = 3200 - 3800 Å Product analysis: VPC	$E_a - E_i$ = 2.7 kcal/mole	a = abstraction i = insertion Energy transfer is less efficient with increasing temperature

Table 1.- Continued

161. $CF_2 + C_2F_4 \rightarrow \text{cyclo-}C_3F_6$

Ref.	Kinetic Methods	Rate Data	Comments
147 Tyerman, et. al. (1969)	T = 298 °K λ = 2490 Å Flash photolysis Product analysis: UV N_2 and N_2O are diluent gases	$A = \frac{1.45 \times 10^{-16}}{T^{1/2}}$ cm^3/mol-s E_a = 3200 ± 625 cal/mole	

162. $^1CH_2 + CH_2Cl_2 \rightarrow CH_2ClCH_2Cl + CH_3CH_2Cl + C_2H_6$

Ref.	Kinetic Methods	Rate Data	Comments
30 Clark, et. al. (1970)	λ = 3000 - 3400 Å Product analysis: GC, GLPC	Steps 4, 5, and 6 produce high vibrational excitation (~90 kcal/mole)	Abstraction predominates Mechanism: 1) $CH_2CO + h\nu \rightarrow {}^1CH_2 + CO$ 2) $^1CH_2 + CH_2Cl_2 \rightarrow 2CH_2Cl$ 3) $^1CH_2 + CH_2Cl_2 \rightarrow CH_3 + CHCl_2$ 4) $2CH_2Cl \rightarrow CH_2ClCH_2Cl^*$ 5) $CH_3 + CH_2Cl \rightarrow CH_3CH_2Cl^*$ 6) $2CH_3 \rightarrow C_2H_6^*$
66 Hassler, et. al. (1966)	λ = 3200 Å T = 298 °K Product analysis: GLPC	Geometric effects in transition state Reaction is at least twice as rapid as $^1CH_2 + CH_3Cl$	Abstraction predominates Mechanism: Steps 3-6 of above mechanism(ref. 30) plus: 1) $CH_2CO + h\nu \rightarrow CH_2 + CO$ 2) $CH_2 + CH_2Cl_2 \rightarrow CH_3 + CHCl_2$ 7) $CH_3 + CHCl_2 \rightarrow CH_3CHCl_2$ 8) $CH_2Cl + CHCl_2 \rightarrow CH_2ClCHCl_2$

Table 1.- Continued

162.	$^1CH_2 + CH_2Cl_2 \rightarrow CH_2ClCH_2Cl + CH_3CH_2Cl + C_2H_6$ (continued)		
Ref.	Kinetic Methods	Rate Data	Comments
66(continued)			9) $2CHCl_2 \rightarrow CHCl_2CHCl_2$ 10) $CH_3 + CHCl_2 \rightarrow CH_2CHCl + HCl$ 11) $CH_2Cl + CHCl_2 \rightarrow C_2H_2Cl_2 + HCl$
163.	$^1CH_2 + C_2H_6 \rightarrow C_3H_8$		
62 Halberstadt, et. al. (1973)	$\lambda = 3130$ Å Product analysis: GC	$k = 4.8 \times 10^{-12}$ cm^3/mol-s	Insertion by direct attack
164.	$CH_2 + 3SO_2 \rightarrow CS_2 + H_2O + S + CO + CO_2$		
73 Hiroaka, et. al. (1974)	$\lambda = 2540$ Å Flow system Product analysis: MS		Mechanism: $CH_2 + SO_2 \rightarrow H_2O + OCS$ $OCS \rightarrow CS_2 + S + CO + CO_2$ (unbalanced)
165.	$CF_2 + NO \rightarrow CF_2NO$		
109 Modica, et. al. (1967)	T = 1600 - 2500 °K Shock tube Product analysis: MS, UV	$A_f = (1.49 \pm 0.33) \times 10^{-10}$ cm^3/mol-s $E_{a,f} = 29200 \pm 3300$ cal/mole $A_r = (3.14 \pm 2.47) \times 10^6$ s^{-1} $E_{a,r} = 20600 \pm 3600$ cal/mole $\Delta H_1 = 4.6$ kcal/mole $\Delta H_f(CF_2NO) = -15.7$ kcal/mole at T = 2000 °K $\Delta H_f(CF_2) = -41.9$ kcal/mole at T = 2000 °K $\Delta H_f(NO) = 21.6$ kcal/mole at T = 2000 °K Mean lifetime of $CF_2NO = 5.61 \times 10^{-5}$ s	f = forward reaction r = reverse reaction At T > 2500 °K, reaction proceeds to equilibrium by: 1) $2CF_2NO \rightarrow 2CF_2O + N_2$ 2) $CF_2NO + NO \rightarrow CF_2O + N_2O$

Table 1.- Concluded.

166.	$CH_2CO + CH_3CH_2Cl \rightarrow$ products		
Ref.	Kinetic Methods	Rate Data	Comments
10 Bamford, et. al. (1968)	Photolysis of CH_2CO to produce CH_2 Product analysis: GC	For $\lambda = 2450 - 4000$ Å, $\frac{k_{Cl}}{k_H} = 1.62$ and $\frac{k_{H1}}{k_{H2}} = 0.098$ For $^1CH_2$: $k_{Cl}/k_H > 16.3$ For $^3CH_2$: $k_{Cl}/k_H < 0.14$ $\Delta H_1 = 40$ kcal/mole Assumption: rates of steps 9 to 11 are equal $k_6 = k_{Cl}$ $k_7 = k_{H1}$ $k_8 = k_{H2}$	$k_H = k_{H1} + k_{H2}$ Relative concentration of $^1CH_2$ is reduced when longer wavelengths and N_2 are present Abstraction mechanism predominates Mechanism: 1) $CH_2CO + h\nu \rightarrow CH_2 + CO$ 2) $CH_2 + CH_2CO \rightarrow C_2H_4 + CO$ 3) $CH_2 + C_2H_4 \rightarrow C_3H_6$ 4) $CH_2 + C_2H_5Cl \rightarrow CH_3CH_2CH_2Cl$ 5) $CH_2 + C_2H_5Cl \rightarrow (CH_3)_2CHCl$ 6) $CH_2 + C_2H_5Cl \rightarrow CH_2Cl + C_2H_5$ 7) $CH_2 + C_2H_5Cl \rightarrow CH_3 + CH_2CH_2Cl$ 8) $CH_2 + C_2H_5Cl \rightarrow CH_3 + CH_3CHCl$ 9) $C_2H_5 + CH_2Cl \rightarrow C_2H_5CH_2Cl$ 10) $CH_3 + CH_2CH_2Cl \rightarrow C_2H_5CH_2Cl$ 11) $CH_3 + CH_3CHCl \rightarrow CH_3CH(CH_3)Cl$ 12) $C_2H_5 + CH_2Cl \rightarrow C_2H_4 + CH_3Cl$ 13) $CH_3 + CH_3CHCl \rightarrow CH_4 + CH_2CHCl$ 14) $C_2H_5 + CH_3CHCl \rightarrow C_2H_6 + CH_2CHCl$ 15) $CH_2Cl + CH_3CHCl \rightarrow CH_3Cl + Cl_2CCHCl$

ANALYSIS OF KINETIC DATA

The kinetic data listed in table 1 were analyzed as follows. The general recommendations were primarily based on the error limits inherent in the methods of measurement of the data. Other criteria which suggest the need for remeasuring rates are the lack of a consistent mechanism and wide variations in data measured by different groups of investigators.

One kinetic method of analysis that requires review is the detection of F_2 by a chemiluminescent titration with Cl_2 or H_2. The titration itself has an inherent error of at least 15 percent.[17-20] Therefore, the rate constants obtained by this method of analysis should be carefully examined.

It is difficult to apply the existing shock tube data to atmospheric reactions. The typical temperature range of a shock tube experiment is 2000 - 4000° K. Therefore, this technique may not yield reliable data for the low-temperature reactions occurring in the troposphere and stratosphere. An entirely different mechanism and set of products may occur in the lower temperature ranges.[127]

The stopped flow method of determining products is generally inadequate in determining the rate data of interest because of the long time between reaction and detection relative to the other kinetic methods. In most cases, the reactions of interest are fast; therefore, fast flow techniques are much better.[64] They tend to minimize the possibility of wall reactions which do not occur in the atmosphere to an appreciable extent.

Flash photolysis is a good method for initiating photolytic gas phase reactions. It is especially good when coupled with a mass spectrometer, the latter being used for determining product distributions. It is usually used to study inorganic reactions.

Kinetic data obtained using a molecular beam mass spectrometer are also fairly reliable for the analysis of reactions in which only a few unique products, that differ appreciably in the molecular weight of the fragments, result. When the molecular weights of the product ions correspond closely, as is often the case in organic reactions, then complex spectra result if mass spectrometry is used alone. The best methods to use for stable product molecules in this case are gas chromatography coupled with mass spectrometry. The gas chromatograph separates compounds with similar molecular weights so that product analysis using mass spectrometry is much more accurate. Infrared or ultraviolet spectroscopy serves to confirm product analysis when used in conjunction with gas chromatography and mass spectrometry. The accuracy of the rate data is questionable when spectroscopic techniques are used alone.

Table 2 lists the best currently available rate data. Rate constants at 298° K were calculated from the Arrhenius rate data for comparison purposes. The units of both the Arrhenius frequency factor and the rate constant are implied by the order of the reaction. Those data that are starred have been judged acceptable; redetermination of the starred rate data is considered unnecessary.

Many of the reactions listed in table 2 have reactants that require photolytic activation to be produced. However, the actual reactions for which the rate data were determined were thermally activated. This is the reason for the tabulation of reaction types.

Rate data for second order reactions for which the rate constants at 298° K were less than or equal to 10^{-18} were accepted even if the methods of obtaining the rate data were questionable. The reasoning for the acceptance of this rate data was that even an error of 10^{3} in the measurements would not appreciably increase the importance of this reaction in the atmosphere; previous workers have determined that second order reactions with rate constants less than 10^{-15} are unimportant.[123]

Table 2.- Rate Data

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	$T(^oK)$	$k_{298\,^oK}$	Reaction Type	Ref.
* 1. $F + F + M \rightarrow F_2 + M$			3	295	8.02×10^{-35}	Thermal	57
* $F_2 + M \rightarrow F + F + M$	7.6×10^{-12}	28.49	2	298	9.66×10^{-33}	Thermal	79, 131, 132
2. $Cl_2 + F_2 + M \rightarrow 2ClF + M$	1.84×10^{-2}	19.8	1.5	298	5.53×10^{-17}	Thermal	50
* 3. $Cl_2 + F \rightarrow Cl + ClF$			2	300	1.1×10^{-10}	Thermal	31
* 4. $F_2 + Cl \rightarrow ClF + F$			2	295	$<1.7 \times 10^{-15}$	Thermal	57
* 5. $F + HCl \rightarrow ClF + H$			2	298	1.2×10^{-11}	Thermal	115
*13. $F_2 + ClO_2 \rightarrow FClO_2 + F$			2	247	1.7×10^{-21}	Thermal	6
*16. $F + PH_3 \rightarrow HF + PH_2$			2	298	$\geq 2.2 \times 10^{-11}$	Thermal	115
*17. $H + F_2 \rightarrow HF + F$		≤ 2.0	2	298	2.5×10^{-11}	Thermal	31
*18. $F + H_2 \rightarrow HF + H$	2.6×10^{-10}	1.60	2	298	1.74×10^{-11}	Thermal	75
19. $H + F + M \rightarrow HF + M$			3	298	2.3×10^{-32}	Thermal	9
24. $F_2 + 2NO + M \rightarrow 2FNO + M$			3	298	7.75×10^{-35}	Thermal	115
25. $F_2NO_3 \rightarrow FO + FNO_3$			1	298	4.8×10^{-8}	Photolytic	24
*27. $2FNO_3 \rightarrow 2FNO_2 + O_2$	1.11×10^{-9}	22.7	2	298	2.49×10^{-26}	Thermal	138
28. $F_2 + 2NO_2 \rightarrow 2FNO_2$	2.7×10^{-12}	10.47	2	298	5.65×10^{-20}	Thermal	113

Table 2.- Continued

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(°K)	k_{298} °K	Reaction Type	Ref.
*30. $NF_2 + F + M \rightarrow NF_3 + M$			3	298	8.9×10^{-31}	Thermal	32
*33. $F + NH_3 \rightarrow HF + NH_2$			2	298	5.5×10^{-13}	Thermal	115
*34. $FO + FO \rightarrow 2F + O_2$			2	298	8.5×10^{-12}	Thermal	32
*35. $F + O_3 \rightarrow OF + O_2$	2.8×10^{-11}	0.450	2	298	1.31×10^{-11}	Thermal	151
*38. $CO + O + M \rightarrow CO_2 + M$	1.63×10^{-32}	4.1	3	298	1.60×10^{-35}	Thermal Low Pressure Limit	139
*41. $F_2 + CO \rightarrow FCO + F$	7.8×10^{-13}	13.5	2	298	9.78×10^{-23}	Thermal	70
*42. $5CH_2O + 6\ O \rightarrow 3H_2 + 3CO + 2H_2O + 2CO_2 + O_2$			2	300	1.5×10^{-13}	Thermal	72
*43. $CH_2O + OH \rightarrow CHO + H_2O$			2	353	1.4×10^{-11}	Photolytic	111
45. $2CH_3O_2 \rightarrow 2CH_3O + O_2$			2	283	2×10^{-15}	Photolytic	93
46. $CH_3O + O_2 \rightarrow CH_2O + HO_2$	1.7×10^{-13}	6.36	2	298	3.68×10^{-18}	Estimated	67
*47. $CH_3O + NO \rightarrow CH_2O + HNO$			2	298	1.0×10^{-14}	Photolytic	102
*48. $CH_3O + NO_2 \rightarrow CH_3ONO_2$			2	298	1.0×10^{-13}	Thermal	68
49. $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$	$\approx 5.25 \times 10^{-13}$	≈ 6.8	2	298	5.40×10^{-18}	Thermal	87
50. $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$			3	298	8×10^{-32}	Estimated	67

2

Table 2.- Continued

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(^oK)	k_{298} ^oK	Reaction Type	Ref.
*51. $CH_4 + OH \rightarrow CH_3 + H_2O$	4.8×10^{-11}	4.97	2	298	1.1×10^{-14}	Thermal	156, 157
*52. $O + CH_4 \rightarrow OH + CH_3$	3.3×10^{-11}	9.2	2	298	5.9×10^{-18}	Thermal	153
*53. $CH_3 + H_2S \rightarrow CH_4 + SH$	4.2×10^{-13}	2.6	2	298	5.2×10^{-15}	Thermal	77, 78
54. $CF_3 + H_2S \rightarrow CHF_3 + SH$	7.7×10^{-14}	3.88	2	298	1.1×10^{-16}	Thermal	4
55. $2CF_3 \rightarrow C_2F_6$	$\geq 6.1 \times 10^{-10}$	≥ 1.5	2	400	9.3×10^{-11}	Thermal	7
$2CH_3 \rightarrow C_2H_6$			2	400	3.88×10^{-11}	Thermal	7
56. $CF + F + M \rightarrow CF_2 + M$			3	298	1.59×10^{-28}	Thermal	110
*57. $O + CH_2{=}CH_2 \rightarrow CH_2O + CH_4 + CH_3CHO + CO + H_2 + O_2$	5.42×10^{-12}	1.130	2	298	8.04×10^{-13}	Photolytic	37
*59. $O(^3P) + CF_2{=}CFCl \rightarrow CF_2O + CFClO + CF_2 + CFCl$	3.9×10^{-11}	2.61	2	298	4.75×10^{-13}	Photolytic	146
*60. $O(^3P) + CF_2{=}CCl_2 \rightarrow CF_2O + CCl_2O + CF_2 + CCl_2$	5.7×10^{-12}	1.29	2	298	6.45×10^{-13}	Photolytic	146
*62. $3CH_2{=}CH_2 + 5CCl_3Br \rightarrow CCl_3CH_2CH_2Br + 2CCl_3CCl_3 + 2CH_2BrCH_2Br$	6.6×10^{-16}	3.20	2	298	2.97×10^{-18}	Photolytic	144
*63. $3CHF{=}CH_2 + 5CCl_3Br \rightarrow CCl_3CHFCH_2Br + 2CHFBrCH_2Br + 2CCl_3CCl_3$	4.18×10^{-16}	5.3	2	298	5.42×10^{-20}	Photolytic	144

Table 2.- Continued

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(°K)	k_{298} °K	Reaction Type	Ref.
*64. $3CH_2{=}CHF + 5CCl_3Br \rightarrow CCl_3CH_2CHFBr + 2CHFBrCH_2Br + 2CCl_3CCl_3$	5.27×10^{-16}	3.30	2	298	2.00×10^{-18}	Photolytic	144
*65. $3CH_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CH_2CF_2Br + 2CH_2BrCF_2Br + 2CCl_3CCl_3$	8.4×10^{-16}	4.60	2	298	3.55×10^{-19}	Photolytic	144
*66. $3CH_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CH_2Br + 2CH_2BrCF_2Br + 2CCl_3CCl_3$	5.3×10^{-16}	8.30	2	298	4.33×10^{-22}	Photolytic	144
*67. $3CHF{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CHFCF_2Br + 2CHFBrCF_2Br + 2CCl_3CCl_3$	3.3×10^{-15}	6.10	2	298	1.11×10^{-19}	Photolytic	144
*68. $3CHF{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CHFBr + 2CHFBrCF_2Br + 2CCl_3CCl_3$	4.2×10^{-15}	7.10	2	298	2.60×10^{-20}	Photolytic	144
*69. $3CF_2{=}CF_2 + 5CCl_3Br \rightarrow CCl_3CF_2CF_2Br + 2CF_2BrCF_2Br + 2CCl_3CCl_3$	2.1×10^{-14}	6.10	2	298	7.05×10^{-19}	Photolytic	144
74. $3C_2H_5Br \rightarrow C_2H_4 + 3HBr + C_2H_3 + C_2H_5$	6.34×10^{11}	46.4	1	298	5.89×10^{-23}	Photolytic	144
*75. $C_2H_6 + F \rightarrow HF + C_2H_5$	1.0×10^{-13}	0.490	2	298	4.36×10^{-12}	Thermal	52
*76. $C_2H_6 + Br \rightarrow C_2H_5 + HBr$	3.26×10^{-11}	12.3	2	298	3.10×10^{-20}	Thermal	33

Table 2.- Continued

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(°k)	k_{298} °K	Reaction Type	Ref.
*77. $C_2H_5F + Br \rightarrow CH_3CHF + HBr$	3.99×10^{-12}	10.3	2	298	1.11×10^{-19}	Thermal	33
*78. $CH_3CHF_2 + Br \rightarrow CH_3CF_2 + HBr$	5.5×10^{-12}	13.3	2	298	9.67×10^{-22}	Thermal	33
*79. $CH_3CF_3 + Br \rightarrow CH_2CF_3 + HBr$	2.5×10^{-11}	22.2	2	298	1.30×10^{-27}	Thermal	33
*80. $CHF_2CHF_2 + Br \rightarrow CHF_2CF_2 + HBr$	9.3×10^{-12}	18.1	2	298	4.93×10^{-25}	Thermal	33
*81. $CF_3CH_2F + Br \rightarrow CF_3CHF + HBr$	9.0×10^{-12}	18.2	2	298	4.03×10^{-25}	Thermal	33
*82. $CF_3CHF_2 + Br \rightarrow CF_3CF_2 + HBr$	2.7×10^{-12}	18.0	2	298	1.69×10^{-25}	Thermal	143
*83. $2CClF_2CClF_2 + F_2 \rightarrow 2ClF + 2CClF_2CF_3$	2.06×10^{2}	36.45	1.5	298	3.80×10^{-25}	Thermal	54
*84. $CF_3CClF_2 + F_2 \rightarrow C_2F_6 + ClF$	81.8	36.52	1.5	298	1.34×10^{-25}	Thermal	54
*87. $F + CHF_3 \rightarrow CF_3 + HF$			2	298	1.9×10^{-13}	Thermal	115
*88. $F_2 + CHF_3 \rightarrow CF_4 + HF$	1.06×10^{-11}	1.04	2	298	1.83×10^{-12}	Thermal	31
*89. $CHF_3 + Br \rightarrow HBr + CF_3$	3.15×10^{-12}	21.1	2	298	1.05×10^{-27}	Thermal	143
*90. $F + CHClF_2 \rightarrow HF + CClF_2$			2	298	2.3×10^{-12}	Thermal	115
*91. $F + CHCl_3 \rightarrow HF + CCl_3$			2	300	5.3×10^{-12}	Thermal	31
92. $F + CHCl_2F \rightarrow HF + CCl_2F$	1.25×10^{-12}	1.29	2	298	1.41×10^{-13}	Thermal	51
*93. $F + CH_2F_2 \rightarrow HF + CHF_2$			2	298	1.1×10^{-11}	Thermal	115

Table 2.- Continued

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(°K)	k_{298} °K	Reaction Type	Ref.
* 94. $Br + CH_2F_2 \rightarrow HBr + CHF_2$	5.5×10^{-12}	15.3	2	298	3.3×10^{-23}	Thermal	143
* 95. $F + CH_2Cl_2 \rightarrow HF + CHCl_2$	2.2×10^{-14}	0.144	2	298	1.7×10^{-14}	Thermal	51
* 96. $F + CH_3F \rightarrow HF + CH_2F$			2	298	8.8×10^{-11}	Thermal	115
* 97. $CH_3F + Br \rightarrow CH_2F + HBr$	1.2×10^{-11}	14.8	2	298	1.67×10^{-22}	Thermal	143
* 98. $F + CH_3Cl \rightarrow HF + CH_2Cl$	5.3×10^{-11}	1.01	2	298	9.6×10^{-12}	Thermal	51
*100. $F + CH_4 \rightarrow HF + CH_3$	5.5×10^{-11}	1.15	2	298	7.89×10^{-12}	Thermal	150
*101. $CH_4 + Br \rightarrow CH_3 + HBr$	2.3×10^{-11}	17.3	2	298	4.7×10^{-24}	Thermal	143
102. $CHCl_3 \rightarrow CCl_2 + HCl$	2.6×10^{11}	4.7	1	298	9.3×10^{7}	Thermal	135
103. $F + CCl_4 \rightarrow CCl_3 + ClF$			2	298	4.0×10^{-16}	Thermal	90
*104. $F_2 + CCl_4 \rightarrow CCl_3F + ClF$	130	28.64	1.5	298	1.28×10^{-19}	Thermal	54
*105. $F_2 + CFCl_3 \rightarrow CF_2Cl_2 + ClF$	40.7	31.49	1.5	298	3.26×10^{-22}	Thermal	54
*106. $F_2 + CF_2Cl_2 \rightarrow CF_3Cl + ClF$	205	34.92	1.5	298	5.01×10^{-24}	Thermal	54
*107. $F_2 + CF_3Cl \rightarrow CF_4 + ClF$	8.18	39.02	1.5	298	1.97×10^{-28}	Thermal	54
*108. $CF_4 + M \rightarrow CF_3 + F + M$		122.421	2	298	5.48×10^{-91}	Thermal	110
110. $CF_3Br + F \rightarrow BrF + CF_3$			2	298	4.0×10^{-15}	Thermal	115
*112. $CCl_3Br + F \rightarrow BrF + CCl_3$	9.3×10^{-11}	≈0	2	298	9.3×10^{-11}	Thermal	17, 18, 19

Table 2.- Continued

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(°K)	k_{298} °K	Reaction Type	Ref.
*114. $CF_3I + F \rightarrow IF + CF_3$	1.2×10^{-10}	≈0	2	298	1.2×10^{-10}	Thermal	17, 18, 19
*115. $CF_3 + M \rightarrow CF_2 + F + M$		92.254	2	298	2.43×10^{-65}	Thermal	110
*116. $CF_3 + CF_3 + M \rightarrow C_2F_6 + M$			3	298	1.16×10^{-31}	Thermal	110
*117. $2CH_3 \rightarrow C_2H_6$			2	298	4.32×10^{-11}	Photolytic	13
*118. $CF_3 + F + M \rightarrow CF_4 + M$		2.849	3	298	7.18×10^{-30}	Thermal	110
*120. $CH_3 + NO \rightarrow CH_3NO$			2	298	4.0×10^{-12}	Photolytic	13
*121. $CH_3 + NO_2 \rightarrow CH_3NO_2$			2	298	5.0×10^{-12}	Photolytic	68
122. $CH_3NO + CH_3 \rightarrow (CH_3)_2NO$			2	298	$>6.6 \times 10^{-14}$	Photolytic	68
123. $CHF_2Cl \rightarrow CF_2 + HCl$	6.9×10^{13}	55.79	1	298	8.3×10^{-28}	Thermal	44, 45
$CF_2 + HCl \rightarrow CHF_2Cl$	9.0×10^{-13}	6.21	2	298	2.51×10^{-7}	Thermal	44, 45
$CF_2 + CF_2 \rightarrow C_2F_4$			2	298	0.345	Thermal	44, 45
$C_2F_4 \rightarrow 2CF_2$	4.6×10^{16}	70.36	1	298	1.14×10^{-35}	Thermal	44, 45
$CHF_2Cl \rightarrow CF_2 + HCl$	4.0×10^{12}	52.80	1	298	7.51×10^{-27}	Thermal	12
$CF_2 + HCl \rightarrow CHF_2Cl$	3.5×10^{-13}	12.12	2	298	4.51×10^{-22}	Thermal	12
124. $CF_3 + CF_3 \rightarrow C_2F_6$			2	298	3.8×10^{-11}	Thermal	6
*131. $CF_2Br + CH_3 \rightarrow CH_3Br + CF_2Br$	1.7×10^{-13}	≈6.4	2	298	3.44×10^{-18}	Thermal	145

Table 2.- Continued

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(°K)	k_{298} °K	Reaction Type	Ref.
*133. $3CHCl_3 \rightarrow CCl_4 + 3HCl + CCl_2{=}CCl_2$	6.3×10^{8}	37.2	1	298	3.27×10^{-19}	Thermal	133
*135. $CBr_4 + CH_3 \rightarrow CH_3Br + CBr_3$	$\approx 2.64 \times 10^{-10}$	≈7.9	2	298	4.24×10^{-16}	Thermal	145
*136. $CCl_4 + CH_3 \rightarrow CH_3Cl + CCl_3$	$\approx 4.21 \times 10^{-11}$	≈12.9	2	298	1.45×10^{-20}	Thermal	145
*138. $CF_3I + CH_3 \rightarrow CH_3I + CF_3$	$\approx 1.05 \times 10^{-10}$	≈7.5	2	298	3.31×10^{-16}	Thermal	145
*139. $CH_3Br + CF_3 \rightarrow CF_3Br + CH_3$	$\approx 3.34 \times 10^{-11}$	12.5	2	298	2.27×10^{-20}	Thermal	145
*143. $CF_2 + M \rightarrow CF + F + M$		106.0	2	298	1.11×10^{-82}	Thermal	107
144. $^1CH_2 + CH_4 \rightarrow {}^3CH_2 + CH_4$			2	298	1.6×10^{-12}	Photolytic	21
145. $CF_2 + CFCl \rightarrow CF_2{=}CFCl$			2	298	$\approx 1 \times 10^{-12}$	Photolytic	147
148. $CF_2 + F + M \rightarrow CF_3 + M$		2.287	3	298	3.72×10^{-26}	Thermal	110
150. $^1CH_2 + CH_4 \rightarrow C_2H_6$			2	298	1.9×10^{-12}	Photolytic	62
*151. $^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2$			2	298	5.3×10^{-11}	Thermal	21
*152. $^1CH_2 + H_2 \rightarrow CH_3 + H$			2	298	7.0×10^{-12}	Thermal	21
*153. $^1CH_2 + H_2 \rightarrow {}^3CH_2 + H_2$			2	298	$<1.5 \times 10^{-12}$	Thermal	21
*154. $^1CH_2 + M \rightarrow {}^3CH_2 + M$ (M = Ar)			2	298	6.3×10^{-13}	Thermal	21
*155. $^3CH_2 + H_2 \rightarrow CH_3 + H$			2	298	$<5 \times 10^{-14}$	Thermal	21

Table 2.- Concluded

Overall Reaction	A of Overall Reaction	E_a of Overall Reaction (kcal/mole)	Order of Overall Reaction	T(^oK)	$k_{298\ ^oK}$	Reaction Type	Ref.
*156. $^3CH_2 + CH_4 \rightarrow 2CH_3$			2	298	$<5 \times 10^{-14}$	Thermal	21
*161. $CF_2 + C_2F_4 \rightarrow$ cyclo-C_3F_6		3.20	2	298	3.8×10^{-20}	Photolytic	147
163. $^1CH_2 + C_2H_6 \rightarrow C_3H_8$			2	298	4.8×10^{-12}	Photolytic	62
165. $CF_2 + NO \rightarrow CF_2NO$	1.49×10^{-10}	29.2	2	298	5.71×10^{-32}	Thermal	109
$CF_2NO \rightarrow CF_2 + NO$	3.14×10^{6}	20.6	1	298	2.44×10^{-9}	Thermal	109

COMMENTS ON SELECTED REACTIONS

The dissociation of fluorine, the reverse of reaction 1, is favored at equilibrium based on the equilibrium constant for reaction 1 which has a value of 8.30×10^{-3} cm^{-3}-mol-s. The rate constant for the reverse reaction was recommended by the authors of reference 132.

Reaction 10, $O_2 + ClF + M \rightarrow O_3$, is an overall reaction which provides a previously unconsidered source of ozone. The possible importance of this reaction should be thoroughly investigated.

The results reported for reaction 17, $H + F_2 \rightarrow HF + F$, in reference 1 are questionable. Photolytic activation was used but the temperature range at which the reaction was studied was too high to avoid interference by the thermally activated reaction.

The rate constants for reaction 18, $F + H_2 \rightarrow HF + H$, appear quite reliable at 300° K since two independent groups of workers, those of references 31 and 75, are in substantial agreement.

A comprehensive review with recommended rate data for nitric oxide reactions is found in reference 68. The reader is referred to this work for detailed data on nitric oxide reactions that are not included in table 1.

Especially important reaction rates, on which reactions 49 ($CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$) and 54 ($CF_3 + H_2S \rightarrow CHF_3 + SH$) are based, are the recombination rates of methyl and trifluoromethyl radicals. Accurate determinations of the temperature dependences of the rate constants for the recombination reactions are needed.

Rate data for reactions 59 and 60 are stated relative to the reaction of $O(^3P) + CF_2{=}CF_2$. The latter reaction has not been well studied.

The decomposition of CCl_4 has been previously discussed with respect to possible sink mechanisms; other than photolysis, no stratospheric sink for CCl_4 has been found.[123] Reaction 102 deserves considerable attention not only as a possible sink mechanism for CCl_4 but also as a mechanism by which substituted methylenes, CHCl and CCl_2, could be formed. Special attention should be placed on an attempt to verify the mechanism of reference 28.

Chlorofluorocarbons, in which there is at least one hydrogen replacing a halogen, have been discussed as a possible replacement for fully halogenated chlorofluorocarbons. Reaction 123, $2CHF_2Cl \rightarrow 2HCl + C_2F_4$, can be used to illustrate the thermal stability of the hydrogen-containing halocarbons. The data from references 12, 44, and 45 vary widely, but the same conclusions may be drawn from all the references. The equilibrium constant for the decomposition of CHF_2Cl has the value of 1.66×10^{-5} cm^{-3}-mol for reference 12 and the value of 3.31×10^{-11} cm^{-3}-mol for references 44 and 45. At equilibrium,the formation of CHF_2Cl is favored. It is then highly unlikely that CHF_2Cl will decompose thermally in the troposphere or stratosphere.

The recombination of two difluorocarbenes, reaction 146, has been studied with little agreement between workers. Both orders and rate constants disagree markedly. For example, references 36 and 147, both studies using flash photolysis, have rate constants at 298° K that differ by a factor of 10^3; the shock-tube measurements of the reverse reaction, references 108 and 26, not only differ in order but also by a factor of 10^{17}. Since this reaction is used as a reference reaction for other relative rate studies, accurate rate data are necessary.

FATE OF FLUORINE BONDS

Hydrogen fluoride is a product rather than a reactant in all reactions surveyed. This is attributed to the large amount of energy that is required to break this bond, 135 kcal/mole.[43] Therefore, no chemical sinks for this compound have been found.

Carbon-chlorine and carbon-hydrogen bonds are broken before carbon-fluorine bonds in all cases examined. No studies of the rates of decomposition of fully substituted chlorofluoromethanes have been reported to date; measurements of the mechanisms and rate data are certainly necessary.

While bonds between fluorine and unlike atoms are relatively strong, the bond in F_2 is very weak in comparison, 35 kcal/mole.[43] Therefore, the concentration of F_2 must be very low in the stratosphere and troposphere. However, both fluorine atoms and diatomic fluorine must be considered as reactive species when compiling reactions from various rate studies. The rate constants for the two species differ, and they must be treated as two distinct reactants.

FUTURE INVESTIGATIONS

The data compiled in table 1 are insufficient so that no concrete conclusions can be drawn about the mechanisms of chlorofluorocarbon decompositions. An important question that must be answered is the fate of the CF_2Cl and $CFCl_2$ radicals when exposed to photolytic energy. Little is known about the energy necessary to break a carbon-chlorine bond to form the substituted carbenes or the absorption cross sections of the radicals.

Methylene, CH_2, has been well studied theoretically using many different types of ab initio and semi-empirical quantum mechanical calculations. A comprehensive review of the calculations is found in reference 85. The substituted carbenes, however, have not received this attention because of the increased sizes of basis sets necessary for the calculations. Increased computer capabilities now make it possible to calculate accurate potential energy surfaces using ab initio methods. Computational studies are useful because of the difficulties encountered in obtaining experimental data on carbene reactions, the high reactivity and short lifetimes of carbenes, and the hazards and difficulties particularly associated with handling fluorinated compounds.

Rowland and Molina[123] have postulated that the most important degradation step for the chlorofluoromethyl radicals is the reaction with diatomic oxygen,

$$CF_2Cl + O_2 \rightarrow CF_2O + ClO \quad .$$

An interesting problem that deserves attention is the structure of the above intermediate and the way it breaks apart to yield ultimate degradation products. One way to study this intermediate is by calculating transition state rate constants for the reaction. A thorough experimental investigation of the chemistry of CF_2O is also indicated since little is known about its absorption spectrum or chemical properties.

Rowland and Molina, in evaluating the reactions of methyl and substituted methyl radicals, use the dissociation energies of the ground state molecules. This is not always correct when photolytic energy is present. In particular, the mechanism for the reactions of the radicals with diatomic oxygen, where the molecules are in the excited states, may not be the same as the ground state reactions. Calculations of the potential energy surfaces are necessary to determine if this assumption is correct.

A large portion of the reactions listed in table 1 cannot be included in stratospheric modeling calculations at the present time because of the lack of measurements of some of the reactant concentrations in the stratosphere. Attempts should be concentrated in making accurate measurements of the reactant concentrations before further modeling of the stratosphere is attempted.

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