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Reactions of ground state chlorine atoms with fluorinated methanes and ethanes

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The reactions of photochemically generated Cl(^2P_J) atoms with a number of fluorohydrocarbons have been investigated in the temperature range 8–95 °C by the competitive photochlorination technique using CH_4 as a primary standard. Relative and absolute rate parameters are reported for CH_3F, CH_2F_2, CH_3CH_2F, CH_2FCH_2F, CH_3CHF_2, CH_3CF_3, CH_2FCHF_2, CHF_2CHF_2, and several auxiliary reactions including CH_3Cl, C_2H_6, and C_3H_8. The internal competition for hydrogen abstraction in asymmetric fluorethanes is examined in detail. The reactivity trends are discussed and it is found that the activation energies in the fluoromethane series correlate with the known C–H bond dissociation energies. The hydrogen reactivity in the fluoroethane series for which a sufficient data base of DH°(C–H) values is not available is best rationalized in terms of inductive effects and resonance interactions.

I. INTRODUCTION

Reactions of ground state chlorine atoms with simple alkanes and alkenes, and some of their chloro derivatives have been extensively studied in the past using competitive techniques. A number of excellent reviews exist.[1–3] This earlier work was motivated by the intrinsic interest in the reactivity of chlorine atoms leading to free radical and chain reaction kinetics, and the desire to test the predictive powers of various theoretical models for this class of reactions.[1,4] More recently, there has been renewed interest, largely in response to environmental concern related to the Cl-catalyzed removal of stratospheric ozone,[5,6] which has led to numerous investigations of Cl (^2P_J) reactions with hydrogen containing compounds of atmospheric interest,[7,8] in as much as these processes convert atomic chlorine into the relatively unreactive reservoir species HCl. These recent studies have largely employed modern "direct" kinetic techniques, and have included the chlorination of chloromethanes[9,10] and chloroethanes[11,12] as a function of temperature. While the direct methods are to be preferred in principle, all techniques which follow the rate of decay of chlorine atoms *only*, have the shortcoming of not being able to distinguish between the reactivity of different types of hydrogens where such distinction is of interest, such as in the case of asymmetric haloethanes. Investigations of Cl atom reactions with fluorohydrocarbons have received much less attention. Yet, the reactivity trends for hydrogen abstraction from analogous partially chlorinated or fluorinated alkanes and their correlation with the corresponding C–H bond dissociation energies are of fundamental and theoretical interest. Manning and Kurylo[10] have investigated the reactions Cl + CH_3Cl and Cl + CH_3F using the flash photolysis-resonance fluorescence technique, and competitive photochlorinations of several fluoroethanes have been reported by Cadman *et al.*,[13] who observed an inert gas effect, and Martens and co-workers.[14] The reported rate parameters in these two studies are not in good agreement, even with respect to internal competition. We have therefore undertaken to examine the reaction of Cl (^2P_J) atoms with a number of fluorinated C_1 and C_2 compounds which complements our recent studies on some chloro-[15–17] and fluoroethanes.[18] In this paper we report on the competitive photochlorinations of CH_3F, CH_2F_2, CH_3CH_2F, CH_3CHF_2, CH_3CF_3, CH_2FCHF_2, and reexamine results[18] on CH_2FCH_2F and CHF_2CHF_2. Also included are some auxiliary results on the photochlorination of CH_3Cl and $(CH_3)_2CH_2$ to provide for internal consistency in comparisons with the earlier data[13,14] on fluorinated ethanes.

II. EXPERIMENTAL

Competitive photochlorinations were carried out in a shielded conventional static apparatus in the temperature range 8–95 °C using filtered light centered at 424 nm. At this wavelength, the chlorine atoms produced by the photolysis of Cl_2 are, for all practical purposes, in their ground electronic state [Cl ($^2P_{3/2}$) > 99%, Cl ($^2P_{1/2}$) < 1%[19]]. The temperature of the reactor was controlled to better than ±0.2 °C and dark reactions were absent as ascertained by repeated blank analyses. Details of the apparatus and experimental procedure have been described elsewhere.[15]

Methane was used as a primary reference, however, in some cases alternative secondary standards were used which included methyl chloride and ethyl chloride. Altogether eight fluorocarbons were investigated or reexamined: CH_3F, CH_2F_2, C_2H_5F, CH_3CHF_2, CH_2FCH_2F, CH_3CF_3, CH_2FCHF_2, and CHF_2CHF_2, which yield eleven corresponding photochlorination products: CH_2FCl,

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CHF_2Cl, and nine mixed fluorochloroethanes, CH_3CHFCl, CH_2ClCH_2F, CH_3CF_2Cl, CH_2ClCHF_2, $CH_2FCHFCl$, CH_2ClCF_3, CH_2FCF_2Cl, $CHFClCHF_2$, and CHF_2CF_2Cl.

Product analyses were carried out by isothermal flame ionization gas chromatography (Hewlett–Packard Model 5830 H) but the temperature setting was varied (80–150 °C) depending on system. Separations were achieved using a 2 m Durapak N (*n*-octane/Porasil C) column. Quantitative analysis involved corrections for the relative sensitivities of the FI detector response, which were presently determined. Light intensity and photolysis times were commensurate with obtaining a sufficient primary photochlorination product yield to achieve high signal accuracy, but below the limit of detection of secondary chlorination products. The same procedures were followed in the case of auxiliary experiments with methyl chloride and *n*-propane.

III. CHEMICALS

All chemicals were obtained commercially: chlorine, methane, ethane, propane, methyl chloride, methyl fluoride, and ethyl chloride from Matheson; difluoromethane, ethyl fluoride, and 1,1,2,2-tetrafluoroethane from PCR Research Chemicals Inc.; 1,1-difluoroethane and 1,2-difluoroethane from ICN Pharmaceuticals, K & K Laboratories; 1,1,1-trifluoroethane from Columbia Organic Chemicals; and 1,1,2-trifluoroethane from Philips Petroleum Co. With the exception of research grade CH_4, which contained no deleterious impurities, all chemicals were purified prior to their use by repeated distillations *in vacuo* at various slush temperatures until free of any detectable amounts of interfering impurities. Trace amounts of residual impurities were innocuous and were tolerated. In general, the purity of the reactants exceeded 99.8%.

IV. RESULTS

In most cases competing reactants were used in at least 20-fold excess over chlorine at total pressures of about 20 Torr. As shown previously in the case of the photochlorination of ethyl chloride,[15] these conditions ensured the validity of the long chain assumption and chain termination predominantly by radical combination. To test if these conditions also apply in the case of the external and/or internal competition in fluorohydrocarbons, a number of experiments were carried out at higher fluorohydrocarbon/Cl_2 ratios and no effect on the product ratios was found. For experimental reasons, in a few experiments dealing with highly reactive reagents (C_3H_8 and C_2H_6), the competitor (CH_4) was used in large excess, while the reactants in question were on the level of, or even below, the chlorine concentration. In order to test the validity of these results a series of experiments was performed with $C_2H_6/C_3H_8/CH_4/Cl_2$ mixtures in which the ratio of hydrocarbons was fixed (with CH_4 in large excess) while the partial pressure of Cl_2 was reduced such that even the more reactive hydrocarbons were in at least 20-fold excess over Cl_2. Again the results obtained for the product ratios did not deviate from those of the other procedure by more than the usual experimental scatter.

For long chains, the observed photochlorination products originate from the propagation reactions which may be represented by the sequence

$$RH + Cl \rightarrow R + HCl, \tag{R1}$$

$$R + Cl_2 \rightarrow RCl + Cl, \tag{R2}$$

where R denotes any of the possible haloalkyl or alkyl radicals. It may be noted that the radicals formed in reaction (R1) are thermal, and hence can neither decompose, nor undergo any internal rearrangement at the temperatures in question. Similarly, the absence of any significant metathetical radical reactions with the parent compounds can be inferred from kinetic data in the literature,[20] as well as the present results which showed no evidence, whatsoever, for this type of reactions.

For internal competition (i.e., CH_3CH_2F, CH_3CHF_2, CH_2FCHF_2) and long chains, the measured product ratio gives the rate constant ratio directly

$$\frac{k}{k'} = \frac{[RCl]}{[R'Cl]}. \tag{1}$$

Since the product ratio can be determined by gas chromatography with great accuracy, internal competition results are inherently most accurate. For competitive photochlorination of RH with a reference compound R'H, the rate constant ratio in terms of the product yields is given by

$$\frac{k}{k'} = \frac{\ln\{1 - [RCl]/[RH]_0\}}{\ln\{1 - [R'Cl]/[R'H]_0\}}, \tag{2}$$

where the subscript 0 denotes initial concentrations. Equation (2) is exact, subject only to the validity of the long chain approximation and the absence of complicating features, such as secondary chlorinations, and/or radical reactions other than with Cl_2. The evaluation of the ratios $[RCl]/[RH]_0$ and $[R'Cl]/[R'H]_0$ in Eq. (2), though possible in principle, is indirect and burdened with some experimental error. It is therefore convenient to rewrite Eq. (2) in the form

$$\frac{k}{k'} = \frac{[RCl][R'H]_0 F}{[R'Cl][RH]_0 F'}, \tag{3}$$

where again $[RCl]/[R'Cl]$ is measured directly, and $[R'H]_0/[RH]_0$ is known from the initial pressure measurements. The factor F (and analogously F') is given by

$$F = 1 + \tfrac{1}{2}\alpha + \tfrac{1}{3}\alpha^2 + \tfrac{1}{4}\alpha^3 + \cdots, \tag{4}$$

where $\alpha \equiv [RCl]/[RH]_0$, or, in terms of the final reactant concentration

$$F = 1 + \tfrac{1}{2}(1-\beta) + \tfrac{1}{3}(1-\beta)^2 + \tfrac{1}{4}(1-\beta)^3 + \cdots, \tag{5}$$

where $\beta \equiv [RH]_f/[RH]_0$. The advantage of Eq. (3) is that the factors F and F' may now be considered as correction factors for higher conversions. Numerical values of the F

TABLE I. F factor as function of conversion.

	$\beta = [RH]_f/[RH]_0$					
	1.00	0.95	0.90	0.80	0.70	0.50
$F(2)$[a]	1.0	1.025	0.050	1.100	1.150	1.250
$F(3)$	1.0	1.026	1.053	1.113	1.180	1.333
$F(4)$	1.0	1.026	1.054	1.115	1.187	1.365
$F(5)$	1.0	1.026	1.054	1.116	1.188	1.377

[a] Number in parenthesis indicates number of terms in Eq. (5).

factors for different conversions are listed in Table I for easy reference. For similar reactivities and very low conversions with respect to both competitors $\alpha \ll 1$, $\alpha' \ll 1$, and Eq. (3) reduces to

$$\frac{k}{k'} = \frac{[RCl][R'H]_0}{[R'Cl][RH]_0}. \tag{6}$$

In practice, Eq. (6) is sufficiently accurate to about 2%–3% conversion, without noticeable error (outside the normal experimental scatter) in the calculated rate constant ratio. Finally, it may be noted that Eqs. (3) and (6) are also valid in the case of simultaneous internal competition against an external standard for each identifiable chlorination product.

For most cases considered in this study Eq. (6) was adequate and was used for data reduction. Corrections were made in the case of some auxiliary experiments where the difference in reactivities between competitors was very large. For example, the ratio of rate coefficients at 298 K for the systems C_3H_8/CH_4 and C_2H_6/CH_4 is about 580 and 550, respectively, and methane was necessarily used in large excess (about 150-fold, a larger excess being undesirable for analytical reasons). Even then, at CH_4 conversions just sufficient to obtain reasonable signals for the reference product CH_3Cl, the depletion in the concentrations of ethane and propane was significant to warrant corrections. In this case the initial concentrations of C_2H_6 and C_3H_8 were sufficiently small to be within the linear response region of the detector, and the ratios $[RCl]/[RH]_f \equiv B$, and hence $\alpha = B/(1 + B)$, could be determined directly.

Over the temperature range of this investigation (8–95 °C) in all cases examined the rate constant ratios conformed to the Arrhenius rate law. The results of the relative measurements on the fluorocarbons listed in Table II are based on the usual least squares treatment, and the stated error limits are one standard deviation. As discussed earlier,[17] the reproducibility of sample preparation rather than the precision of gas-chromatographic analyses was the accuracy limiting factor. Therefore, at least two, but usually three different reagent mixtures were prepared for each system investigated. The random errors, accountable for the error limits quoted in Table II under the headings A_i/A_j and $(E_j - E_i)/\mathrm{R}$, include uncertainties in pressure measurements in the preparation of gas mixtures, varying levels of impurities from one mixture to another, and from one sample to another, possible deviations from homogeneity in gas sampling (if any), and errors in gas-chromatographic peak area determinations.

The main source of the systematic errors, if not accounted for, are the differences in the FI detector response towards the compounds of interest. These differences were found to be unexpectedly large. Since, of the 11 chlorofluorohydrocarbons determined only four authentic samples were available to us, interpolation procedures were developed to yield the missing data. It was found that remarkably linear relationships exist between the correction factors for detector sensitivity and the retention times of compounds with analogous F, Cl

TABLE II. Relative Arrhenius parameters for H-atom abstraction by chlorine atoms.[a]

Competitors R_iH/R_jH	A_i/A_j[b]	$(A_i/A_j)_{corr}$[c]	$(E_i - E_j)/\mathrm{R}$ (K)
CH_3F/CH_4	$1.16_2 \pm 0.027$	2.29 ± 0.11[d]	-190 ± 6
CH_2F_2/CH_4	0.508 ± 0.020	1.51 ± 0.06	228 ± 12
$CH_3C\underline{H}_2F/CH_4$	$3.27_3 \pm 0.17_4$	1.60 ± 0.09[d]	-1113 ± 16
$C\underline{H}_3CH_2F/CH_4$	$1.78_6 \pm 0.100$	1.26 ± 0.09	-515 ± 17
$CH_3C\underline{H}F_2/CH_3C\underline{H}_2Cl$	0.586 ± 0.032	$0.51_2 \pm 0.03$	583 ± 17
$CH_3C\underline{H}F_2/C\underline{H}_3CH_2Cl$	0.769 ± 0.037	$0.63_5 \pm 0.03$	176 ± 15
$C\underline{H}_3CHF_2/CH_3C\underline{H}_2Cl$	0.550 ± 0.042	$0.60_0 \pm 0.05$[d]	2012 ± 23
$C\underline{H}_3CHF_2/C\underline{H}_3CH_2Cl$	0.654 ± 0.038	$0.67_1 \pm 0.04$[d]	1578 ± 18
$CH_2FCH_2F/CH_3C\underline{H}F_2$	$3.63_2 \pm 0.13$	$4.49_3 \pm 0.20$[d]	100 ± 11
$CH_2FC\underline{H}F_2/CH_4$	0.888 ± 0.040	$0.50_0 \pm 0.02$[d]	206 ± 14
$C\underline{H}_2FCHF_2/CH_4$	$1.05_1 \pm 0.045$	$0.70_0 \pm 0.04$[d]	315 ± 13
CH_3CF_3/CH_4	$1.87_2 \pm 0.18_6$	1.05 ± 0.11	2479 ± 29
$CHF_2CHF_2/CH_3C\underline{H}F_2$	0.728 ± 0.050	1.09 ± 0.08[d]	1479 ± 20

[a] Statistical A-factor ratios (not reduced on a per atom basis). Stated uncertainty limits are $\pm 1\sigma$.

[b] A-factor ratios not corrected for the relative FI detector sensitivities.

[c] Corrected A-factor ratios using data from Table III. $(A_i/A_j)_{corr} = (A_i/A_j) \times (CF)_i/(CF)_j$.

[d] Value based on estimated correction factor (CF) for one of the products (Table III).

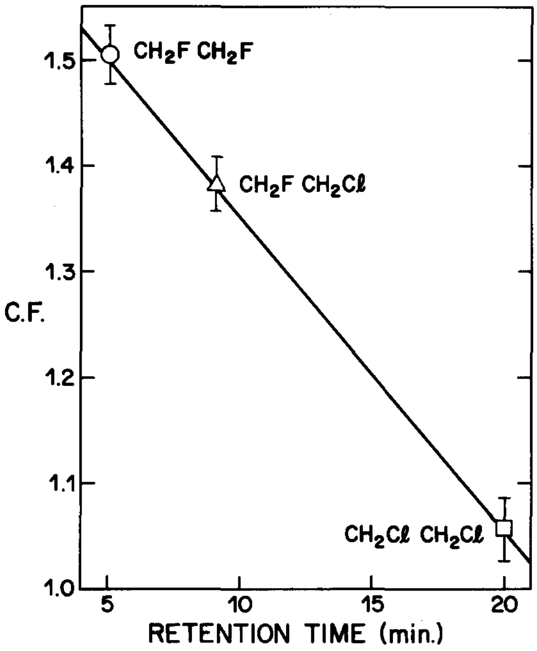

FIG. 1. Relationship between the correction factor CF for the relative FID sensitivity (Table III) and retention time; Durapak N column under isothermal conditions at 80 °C.

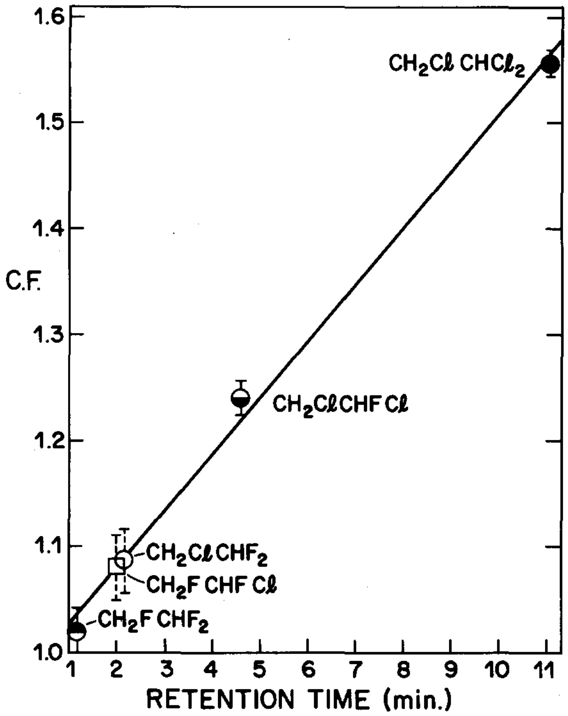

FIG. 2. Relationship between the CF correction factor and retention time; Durapak N column under isothermal conditions at 110 °C.

substitution. Two examples of such linear behavior are shown in Figs. 1 and 2. Applying a "bracketing" method, the correction factors (CF) for all compounds of interest were estimated as shown in Table III. These relative correction factors are independent of temperature over the range 80–150 °C covered in our analyses, provided isothermal conditions are maintained during any given

TABLE III. Correction factors for the relative sensitivity of the flame ionization detector towards F, Cl-substituted hydrocarbons of interest.

Experimental data[b]		Auxiliary experimental data	
Compound	CF[a]	Compound	CF
CH_3CHCl_2 (reference)	1	CH_3Cl	1.960 ± 0.030
CHF_2Cl	5.838 ± 0.094	CH_2F_2	4.22 ± 0.13
CH_2FCH_2Cl[c]	1.383 ± 0.025	CH_2Cl_2	2.66 ± 0.065
CH_3CF_2Cl	0.873 ± 0.005	CH_3CH_2Cl	0.989 ± 0.011
CF_3CH_2Cl	1.103 ± 0.010	CH_3CHF_2[c]	0.948 ± 0.008
		CH_2FCH_2F	1.507 ± 0.028
Estimates		CH_2ClCH_2Cl	1.057 ± 0.013
		CH_2FCHF_2	1.020 ± 0.023
CH_2FCl[d]	3.87 ± 0.15	$CH_2ClCHFCl$	1.240 ± 0.014
CH_3CHFCl[e]	0.96 ± 0.02	$CH_2ClCHCl_2$	1.571 ± 0.009
CHF_2CH_2Cl[f]	1.08_5 ± 0.03	CHF_2CHF_2[c]	1.356 ± 0.016
$CH_2FCHFCl$[f]	1.08 ± 0.03	$CHFClCHFCl$	1.407 ± 0.031
CHF_2CHFCl[g]	1.30 ± 0.06	CH_2ClCF_2Cl	1.043 ± 0.009
CH_2FCF_2Cl[h]	1.10 ± 0.01	CH_2FCF_3	1.071 ± 0.007
CHF_2CF_2Cl[i]	1.31 ± 0.05	CH_2ClCF_3	1.103 ± 0.010
		$CHCl_2CF_3$	1.099 ± 0.020
		$CH_3CHClCH_3$	0.603 ± 0.006
		$CH_3CH_2CH_2Cl$	0.714 ± 0.008

[a] The correction factor is defined in terms of the relative sensitivities (S) as: CF(RX) = $S(CH_3CHCl_2)/S(RX)$.

[b] Calibrations against methyl chloride unless stated otherwise.

[c] Calibrated against 1,1-dichloroethane.

[d] Linear interpolation between CH_2F_2 and CH_2Cl_2.

[e] Linear interpolation between CH_3CHF_2 and CH_3CHCl_2.

[f] Linear interpolation between CH_2FCHF_2, $CH_2ClCHFCl$, and $CH_2ClCHCl_2$ (Fig. 2).

[g] Arithmetic mean of two linear interpolations between CHF_2CHF_2 and $CHFClCHFCl$ yielding CF(CHF_2CHFCl) = 1.36 ± 0.03, and CHF_2CHF_2 and CH_2ClCF_2Cl yielding CF(CHF_2CHFCl) = 1.24 ± 0.03.

[h] Linear interpolation between CH_2FCF_3 and CH_2ClCF_3.

[i] Linear interpolation between CHF_2CHF_2 and $CHCl_2CF_3$.

analysis. The sensitivity corrections which affect the preexponential factor ratios but not the activation energy differences have been accounted for in Tables II and IV under the entry $(A_i/A_j)_{\rm corr}$.

If the relative measurements are to yield absolute rate parameters a reliable standard is needed. In two earlier competitive studies of the photochlorination of C_2H_5F, CH_3CHF_2[13,14] and CH_3CF_3,[13] indirectly determined values of the rate constants for propane,[13] and methyl chloride[14] were used as a reference, while the absolute rate parameters for the chlorination of CH_3CHF_2, CH_2FCH_2F, and CHF_2CHF_2 reported recently from this laboratory[18] were based on the value for $k(Cl + C_2H_6)$ determined by Lewis *et al.*[21] using the low pressure discharge flow-resonance fluorescence (DF–RF) technique. In the present work the chlorination of methane was chosen as a primary standard. Not only is this reaction now one of the best studied in gas phase kinetics,[7,8,20] but unlike CH_3Cl, and particularly $(CH_3)_2CH_2$ and C_2H_6, methane is relatively unreactive toward chlorine atom attack and therefore better suited for relative rate measurements involving at least some of the fluorohydrocarbons. Consistent with our previous investigations,[15–17] we adopted the absolute rate constant value ($cm^3\ s^{-1}$) determined by Keyser[22]

$$k_{CH_4} = (1.65 \pm 0.32) \times 10^{-11} \times \exp[-(1530 \pm 68)/T] \qquad (7)$$

for the temperature range 291–423 K using the direct DF–RF technique. While this choice may be debatable, we consider this value to be more appropriate for our range of temperatures than that recommended by the NASA panel[8] for the range 200–300 K which corresponds to stratospheric temperatures. Moreover, experimental evidence for the retention of Keyser's value has been presented elsewhere.[16] Absolute rate parameters for fluorohydrocarbons based on Eq. (7) are presented in Table V.

In order to permit a meaningful comparison with the photochlorination results of Cadman *et al.*[13] and Martens *et al.*,[14] a series of auxiliary experiments on methyl chloride and propane were carried out and the results for the relative Arrhenius parameters are shown in Table IV. Also included, for internal comparison, are our recent determinations of the relative rates for ethyl chloride[17] and ethane[16] against CH_4. Absolute rate parameters for these auxiliary reactions based on Eq. (7) are collected in Table VI and compared with some literature values.

TABLE IV. Relative rate parameters for H-atom abstraction by chlorine atoms for reference reactions.[a]

Competitors R_iH/R_jH	$(A_i/A_j)_{\rm corr}$[b]	$(E_i - E_j)/R$ (K)	Ref.
$CH_3Cl/CH_3C\underline{H}_2Cl$	1.25 ± 0.05	796 ± 8	this work
$CH_3Cl/C\underline{H}_3CH_2Cl$	$1.45_5 \pm 0.05$	384 ± 8	this work
$CH_3C\underline{H}_2Cl/CH_4$	$1.42_2 \pm 0.02_6$	-1114 ± 3.0	17
$C\underline{H}_3CH_2Cl/CH_4$	$1.29_5 \pm 0.02_9$	-684 ± 3.4	17
C_2H_6/CH_4	7.33 ± 0.38	-1298 ± 15	16
$(CH_3)_2C\underline{H}_2/CH_4$	$4.92_5 \pm 0.24$	-1444 ± 14	this work
$(C\underline{H}_3)_2CH_2/CH_4$	$6.80_5 \pm 0.33$	-1318 ± 13	this work
$CH_3C\underline{H}F_2/C_2H_6$	$0.08_4 \pm 0.00_6$	865 ± 25	18

[a] Stated uncertainty limits reflect both precision of competitive experiments and the uncertainty ($\pm 1\sigma$) in the determination of correction factors for the sensitivity of the flame ionization detector.

[b] Statistical *A*-factor ratio.

TABLE V. Absolute rate parameters for H-atom abstraction by chlorine atoms from fluorohydrocarbons.[a,b]

Reactant	$10^{11} \times (A/cm^3\ s^{-1})$	E/R (K)	$10^{13} \times (k_{298}/cm^3\ s^{-1})$
CH_3F	3.78 ± 0.75	1340 ± 68	4.21 ± 1.27
CH_2F_2	2.49 ± 0.49	1758 ± 69	$(6.83 \pm 2.08) \times 10^{-1}$
$CH_3C\underline{H}_2F$	2.64 ± 0.53	417 ± 70	$(6.51 \pm 2.02) \times 10$
$C\underline{H}_3CH_2F$	2.08 ± 0.42	1015 ± 70	6.90 ± 2.14
$CH_3C\underline{H}F_2$	1.20 ± 0.24	999 ± 70	4.20 ± 1.30[c]
	1.35 ± 0.27	1022 ± 70	4.37 ± 1.36[d]
	$1.27_5 \pm 0.27$	1011 ± 70	4.29 ± 1.33[e]
$C\underline{H}_3CHF_2$	1.41 ± 0.30	2429 ± 72	$(4.06 \pm 1.30) \times 10^{-2}$ [c]
	1.43 ± 0.29	2424 ± 70	$(4.19 \pm 1.30) \times 10^{-2}$ [d]
	1.42 ± 0.29	2427 ± 71	$(4.13 \pm 1.30) \times 10^{-2}$ [e]
CH_2FCH_2F	5.73 ± 1.24	1111 ± 71	$(1.38 \pm 0.44) \times 10$[f]
$CH_2FC\underline{H}F_2$	0.825 ± 0.16	1736 ± 69	$0.24_3 \pm 0.07_4$
$C\underline{H}_2FCHF_2$	$1.15_5 \pm 0.23$	1845 ± 69	$0.23_6 \pm 0.07_2$
CH_3CF_3	1.73 ± 0.38	4009 ± 74	$(2.49 \pm 0.83) \times 10^{-4}$
CHF_2CHF_2	1.39 ± 0.31	2490 ± 73	$(3.27 \pm 1.09) \times 10^{-2}$ [f]

[a] Based on the reaction $CH_4 + Cl \rightarrow CH_3 + HCl$ as a primary standard, $k_r/cm^3\ s^{-1} = (1.65 \pm 0.32) \times 10^{-11} \exp[-(1530 \pm 68)/T]$ (Ref. 22).

[b] Stated uncertainties in Arrhenius parameters ($\pm 1\sigma$) allow for error limits of the reference reaction. *A* factors reported refer to the total H abstraction of a given type.

[c] Based on rate parameters for the reaction $CH_3C\underline{H}_2Cl + Cl \rightarrow CH_3CHCl + HCl$ as secondary reference (Tables IV and VI).

[d] Based on rate parameters for the reaction $C\underline{H}_3CH_2Cl + Cl \rightarrow CH_2CH_2Cl + HCl$ as secondary reference (Tables IV and VI).

[e] Arithmetic mean of values in Ref. c and d.

[f] Based on the reaction $CH_3C\underline{H}F_2 + Cl \rightarrow CH_3CF_2 + HCl$ as secondary reference using the arithmetic mean values of the rate parameters.

V. DISCUSSION

A. General trends

Inspection of Table V reveals several features: (i) in the case of fluoroethanes the activation energy increases for both α- and β-hydrogen abstraction with progressive fluorine substitution on the same carbon; (ii) for asymmetrical molecules the attack of chlorine is faster and the activation energy lower at the more fluorinated site; (iii) the highest activation energy and lowest rate is observed in the case of CH_3CF_3, the most polar molecule in the series. These trends parallel those observed for the α-substituted chloroethanes: CH_3CH_2Cl, CH_3CHCl_2, CH_3CCl_3[16]; (iv) substitution of fluorine in the vicinal (β) position is less clear, thus the activation energy for hydrogen abstraction in CH_2FCH_2F is somewhat higher than that for the primary hydrogen in $C\underline{H}_3CH_2F$, while the abstraction of secondary hydrogen in $C\underline{H}_2FCHF_2$ and primary hydrogen in $C\underline{H}_3CHF_2$ shows a reverse trend, the activation energy being substantially lower in the former. Further fluorine substitution on the adjacent carbon atom results again in a higher activation energy when one compares CHF_2CHF_2 with $C\underline{H}_2FCHF_2$, but

TABLE VI. Absolute rate parameters for H-atom abstraction by Cl atoms for reference reactions.

Reactant	$10^{11} \times (A/$ cm^3 s$^{-1})$[a]	E/R (K)	$10^{12} \times (k_{298}/$ cm^3 s$^{-1})$	Ref.
CH_3Cl	2.93 ± 0.58	1213 ± 68	$0.50_1 \pm 0.15_2$	this work[b]
	3.11 ± 0.62	1229 ± 69	$0.50_2 \pm 0.15_2$	this work[c]
	3.36 ± 0.71	1250 ± 57	$0.50_7 \pm 0.14_4$	10[d]
	21.2 ± 4.3	1787 ± 69	$0.52_7 \pm 0.15$	9[e]
	5.63	1661	0.21_4	14[f]
	3.4	1260 ± 200	0.49	8[g]
$CH_3C\underline{H}_2Cl$	2.35 ± 0.46	417 ± 68	$5.95 \pm 1.7_7$	17[h]
$C\underline{H}_3CH_2Cl$	2.14 ± 0.42	846 ± 68	1.28 ± 0.38	17[h]
C_2H_6	12.1 ± 2.4	232 ± 70	55.5 ± 17.2	16[h]
	9.5_6	413	23.9	13[i]
	9.01 ± 0.48	133 ± 15	56.7 ± 4.2	21[j]
	7.7	90 ± 90	57	8[g]
$(CH_3)_2C\underline{H}_2$	$8.13 \pm 1.6_2$	86 ± 69	60.9 ± 18.7	this work[h]
	7.08	221	33.7	13[i]
$(C\underline{H}_3)_2CH_2$	11.2 ± 2.24	212 ± 69	55.0 ± 16.7	this work[h]

[a] Statistical *A* factors.

[b] From competition with $CH_3C\underline{H}_2Cl$ (Table IV) and primary standard CH_4 [Eq. (7)].

[c] From competition with $C\underline{H}_3CH_2Cl$ (Table IV) and primary standard CH_4 [Eq. (7)].

[d] Direct determination using FP–RF technique.

[e] Direct determination using DF–MS technique.

[f] Used as reference reaction by Martens *et al.* (Ref. 14).

[g] Recommended value by the NASA panel for stratospheric temperatures (200–300 K).

[h] From competition with CH_4 (Table IV) and Eq. (7).

[i] Used as reference reaction by Cadman *et al.* (Ref. 13).

[j] Direct determination using low pressure DF–RF technique.

the difference in activation energies is only marginal between CHF_2CHF_2 and $C\underline{H}_3CHF_2$. The preexponential factors in the fluoroethanes are lower than the corresponding values for primary, secondary, and tertiary hydrogens in the alkanes. However, a clear-cut trend within the fluoroethane series is not discernable. This may not be surprising since the sensitivity correction factors for six of the nine chlorination products were estimated by interpolation.

Turning to the fluoromethanes our results indicate that the activation energy increases and the preexponential factor decreases with additional fluorine substitution in going from CH_3F to CH_2F_2. Thus, while the activation energy for the chlorination of CH_3F is less than for the reference compound CH_4, it is higher in the case of CH_2F_2. This trend is consistent with the competitive photochlorination data on CHF_3 reported by Coomber and Whittle[23] and parallels the C–H bond dissociation energies in the fluoromethane series. We return to this point later in the discussion.

B. Internal competition

The results for the internal competition in CH_3CH_2F, CH_3CHF_2, and CH_2FCHF_2, respectively, are presented in Table VII, and compared with the available data from the literature. Cadman *et al.*[13] studied the internal competition in CH_3CH_2F and CH_3CHF_2 in the absence and presence of C_2F_6, and found in the case of CH_3CHF_2 a significant inert gas effect, while none was observed in this laboratory.[18] In fact, our values for the activation energy differences for the abstraction of primary and secondary hydrogen in CH_3CH_2F, and primary and tertiary hydrogen in CH_3CHF_2 are in excellent agreement with the data of Cadman *et al.*, in the presence of excess C_2F_6. The agreement for the *A*-factor ratios is deemed also reasonable, noting that the sensitivities of the detector response towards the respective chlorination products were assumed to be equal[24] in Ref. (13). The absolute Arrhenius parameters reported by Cadman *et al.* were based on the photochlorination of C_2H_5F/C_3H_8 mixtures in the presence of C_2F_6, using the abstraction of secondary hydrogen in propane as a reference. The rate parameters used for the latter reaction are no longer tenable. A recalculation of their data using the rate constant for $(CH_3)_2C\underline{H}_2$ determined in this study is shown in Table VII. Within the experimental error, the activation energies, but not the *A* factors, agree with the present determinations. Martens *et al.*[14] studied the photochlorination of the same compound at about 360 nm in a flow system with CH_3Cl as competitor and He as diluent. As can be seen from Table VII their results for the internal competition, particularly in the case of CH_3CHF_2, are not in good agreement with either those of Cadman *et al.* or the present study. The absolute rate parameters of Martens *et al.* were based on the original indirect Arrhenius expression for the chlorination of CH_3Cl reported by Knox,[25] leading to significantly higher activation energies. However, if the relative rate data are recalculated using the rate constant value for CH_3Cl determined in this work, the agreement achieved is within experimental error with the exception of the preexponential factor for CH_3CHF_2. The results of all three studies underline the large increase in the activation energy difference with

TABLE VII. Rate parameters for internal competition[a]

Reactant	A_α/A_β	$\frac{A_\alpha/n_\alpha}{A_\beta/n_\beta}$ [b]	$(E_\beta - E_\alpha)$	$10^{11} \times A_\alpha$	$10^{11} \times A_\beta$	E_α	E_β	Ref.
$\overset{\beta}{C}H_3\overset{\alpha}{C}H_2F$	1.48 ± 0.06	2.22 ± 0.09	1151 ± 26	1.09	0.74	894	2045	13[c]
	1.45 ± 0.11	2.18 ± 0.17	1165 ± 48					13[d]
				1.24 ± 0.32	0.84 ± 0.22	625 ± 171	1776 ± 173	13[e]
	2.14 ± 0.05	3.21 ± 0.08	995 ± 22	6.76	3.16	1950	2945	14[f]
				3.74 ± 0.76	1.75 ± 0.35	1093 ± 139	2087 ± 137	14[g]
	1.27 ± 0.08	1.90 ± 0.12	1188 ± 17	2.64 ± 0.53	2.08 ± 0.42	829 ± 139	2017 ± 139	this work
$\overset{\beta}{C}H_3\overset{\alpha}{C}HF_2$	0.63_1 ± 0.03	1.89 ± 0.03	2917 ± 31	0.26_8	0.42_5	1944	4861	13[c]
	0.34_5 ± 0.06	1.04 ± 0.19	3339 ± 115					13[d]
				0.306 ± 0.08	0.48_5 ± 0.13	1675 ± 176	4592 ± 180	13[e]
	1.48 ± 0.03	4.44 ± 0.09	2425 ± 15	1.51	1.02	2980	5405	14[f]
				0.83_7 ± 0.17	0.56_6 ± 0.11	2122 ± 137	4546 ± 137	14[g]
	0.90 ± 0.08	2.70 ± 0.24	2814 ± 52	1.27_5 ± 0.27	1.42 ± 0.29	2008 ± 139	4822 ± 141	this work
$\overset{\beta}{C}H_2F\overset{\alpha}{C}HF_2$	0.71 ± 0.06	1.42 ± 0.12	216 ± 38	0.82_5 ± 0.16	1.15_5 ± 0.23	3450 ± 137	3666 ± 137	this work

[a] Stated uncertainties are ±1σ. Those referring to the absolute Arrhenius parameters include the error limits for the reference reaction. Units for A are $cm^3\ s^{-1}$; units for E are cal mol^{-1}.

[b] Per available C–H bond.

[c] Experiments in presence of C_2F_6. Absolute rate parameters based on the reference reaction Cl + $(CH_3)_2C\underline{H}_2$ reported in Ref. 13 (cf. Table VI).

[d] Experiments in the absence of C_2F_6.

[e] Experiments in presence of C_2F_6. Absolute rate parameters recalculated based on the reference reaction Cl + $(CH_3)_2C\underline{H}_2$ reported in this work (Table VI).

[f] Absolute rate parameters based on the reference reaction Cl + $CH_3Cl \rightarrow CH_2Cl$ + HCl reported in Ref. 14 (cf. Table VI).

[g] Absolute rate parameters recalculated based on reference reaction Cl + $CH_3Cl \rightarrow CH_2Cl$ + HCl determined in this work against $C\underline{H}_3CH_2Cl$ (Table VI).

increasing fluorination on the same carbon atom, while our result on CH_2FCHF_2 emphasizes the existence of a compensating effect with fluorine substitution in the vicinal group.

C. Activation energy versus bond dissociation energy

Table VIII lists activation energies and C–H bond dissociation energies for the chloro- and fluoromethanes and some of the ethanes. In the case of the F, Cl-substituted methane series fairly accurate bond dissociation energies are now available. Pickard and Rodgers[26] reported the D°H(C–H) values for all the fluoromethanes, while Weissman and Benson[27] have published the corresponding values for the chloromethanes. The pattern which emerges shows a clear correspondence between the activation and C–H bond energies. For the fluoromethanes both E_a and D°H(C–H) increase with progressive fluorine substitution, while just the opposite trend is observed for the chloromethanes. The reasons for this behavior must reside in electronic effects. In both series the substitution of the first halogen lowers E_a and D°H(C–H) in relation to the hydrocarbon analog CH_4. In this connection it may be noted that the activation energies for CH_4 and the chlorinated methanes determined by Clyne and Walker[9] using a discharge flow–mass spectrometric technique may be subject to a systematic error[8,10] since their activation energies for CH_4 and CH_3Cl are uniformly higher than those determined directly by Manning and Kurylo[10] using the FP–RF technique, however the activation energy differences (for CH_4 and CH_3Cl) are in good agreement between these two studies. Nevertheless, the work of Clyne and Walker represents the only direct kinetic determination of the chloromethane series, and their results taken collectively, provide a good basis for comparison with the D°H(C–H) values. On the other hand, while the activation energy for CH_3Cl reported by Manning and Kurylo is in excellent agreement with that reported in the present study, our results differ very significantly in the case of CH_3F. We have no ready explanation for this discrepancy.

In the case of the fluoroethanes, and especially chloroethanes, a sufficient data base of "measured" C–H bond energies is not available to establish a definite correspondence with the reactivity of hydrogen towards Cl-atom attack. Still, the cited D°H(C–H) values taken from a recent review by McMillen and Golden[28] do suggest the existence of a trend, this is particularly apparent in the case of CH_3CF_3 which has the highest activation energy for H abstraction and a C–H bond strength equal to that in CF_3H. Martens *et al.*[14] have pointed out that in the case of chlorinated ethanes the activation energies do not follow an Evans–Polanyi[1,29] type of a relationship, while such a relationship could work in the chlorination of fluoroethanes. Yet the activation energies for the fluoro

TABLE VIII. Comparison of activation energies for H abstraction by chlorine atoms with corresponding C–H bond dissociation energies.[a]

Compound	DH°_{298}	Ref.	E_a	Ref.	Compound	DH°_{298}	Ref.	E_a	Ref.
CH_4	105.1	27	3040	22					
			3560	9					
			2529	10					
CH_3F	101.3	26	1535	10	CH_3Cl	102.9	27	3551	9
			2663	b				2443	b
								2550	c
								2484	10
CH_2F_2	103.2	26	3493	b	CH_2Cl_2	100.6	27	2878	9
								2165	d
CF_3H	106.7	26	7570	23	$CHCl_3$	95.2	27	2741	9
C_2H_6	98.2	28	461	16					
			264	21					
$CH_3C\underline{H}_2F$			829	b	$CH_3C\underline{H}_2Cl$			828	17
$CH_3C\underline{H}F_2$	99.5	28	2008	b	$CH_3C\underline{H}Cl_2$			1264	16
$C\underline{H}_3CH_2F$			2017	b	$C\underline{H}_3CH_2Cl$			1681	17
$C\underline{H}_3CHF_2$			4822	b	$C\underline{H}_3CHCl_2$			2784	16
CH_3CF_3	106.7	28	7967	b	CH_3CCl_3			4115	16
			~6000	e				>2400	f
C_2F_5H	102.7	28	4490	23	C_2Cl_5H	95	28	<2940	g

[a] Units of DH°_{298} are in kcal mol^{-1}; units of E_a in cal mol^{-1}.

[b] This work.

[c] H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **76**, 1201 (1954), based on $k(CH_3Cl)/k(CH_4)$ reevaluated using $k(CH_4)$ from Ref. 22.

[d] From relative $k(CH_2Cl_2)/k(CH_4)$ in Ref. 25 recalculated using $k(CH_4)$ from Ref. 22.

[e] From Ref. 13, only approximate value was determined.

[f] From Ref. 12, only lower limit was determined.

[g] C. Cillien, P. Goldfinger, G. Huybrechts, and G. Martens, Trans. Faraday Soc. **63**, 1631 (1967), based on $k(C_2Cl_5H)/k(CHCl_3)$ recalculated using $k(CHCl_3)$ from Ref. 9.

and chloro analogs in the ethane series show qualitatively similar trends, the activation energies in the case of the fluorides being consistently somewhat higher (Table VIII). There is definitely a need for further experimental D°H(C–H) bond dissociation energies in this series of compounds before the activation parameters can be fully understood.

D. Further interpretation

Attempts to explain the reactivity trends for chlorine atom attack in chloro- and fluorohydrocarbons have been made in the literature. The influences of inductive effects, electronegativity arguments, resonance interactions, steric effects, van der Waals repulsion, attractive interactions due to dispersion forces, dynamic effects, as well as electronic effects have been invoked. Thus, to explain the generally lower hydrogen reactivity in CH_3CH_2Cl compared with C_2H_6, Wijnen and co-workers[30] proposed that the incident chlorine atom is repelled by the Cl atom in the molecule. Though it would appear that such a repulsion should be more pronounced at the chlorinated site, the attack on the methylene group in CH_3CH_2Cl has been confirmed[15,17] to be much faster. A plausible explanation advanced by Wijnen *et al.*[30] is that the difference in rates is due to the electron withdrawing power of the highly electronegative Cl atom: the electrons are drawn towards the Cl atom, thus weakening the C–H bonds in the CH_2Cl group relative to the methyl group in CH_3CH_2Cl. Arguments to the same effect have been made by Wine and Semmes[12] who speculated further, that the substitution of Cl on one carbon atom not only weakens the geminal C–H bonds, but also strengthens the C–H bonds on the adjacent carbon. On the other hand, it is generally accepted that substitution of one or more halogens in the 1-position deactivates the hydrogens towards further attack by an electrophilic reactant such as Cl, in the vicinity of the halogen(s), this effect decreasing with increasing separation.[31–34] If this inductive effect was the only one operative, one would expect the deactivation in the 2 position to be smaller, in disagreement with our observation and those of others.[13,14] Evidently, the behavior of chloro- and fluoroethanes toward Cl-atom attack is different from that, for example, of the 1-chlorobutanes,[31] and other considerations must enter.

An alternative interpretation has been presented by Johnston and Goldfinger[4] to explain the failure of the London–Polanyi–Eyring–Sato (LEPS) and bond-energy–bond-order (BEBO) method in predicting the observed trend in activation energy with bond energy for chlorine-atom attack on hydrogen in chlorinated methanes and ethanes. Seeking an explanation in terms of nonbonding interactions between the incident and bound chlorine atom(s) in the molecule, Johnston and Goldfinger[4] evaluated the Lennard-Jones 6-12 potential function for intermolecular interaction of chlorine atoms, and showed, that for the dimensions of their activated complexes the interactions were on the attractive part of the potential. Accordingly, the authors concluded that the observed activation energies were not to be ascribed to van der Waals repulsions, but to dynamic effects involving dispersion forces which result in the preferential attraction between the bound and free chlorine atoms.

As the dispersion forces are directly related to the polarizabilities of the bound atoms, such preferential attraction should be absent in the case of chlorine atom attack on fluorohydrocarbons since the polarizability[35] of fluorine is even less than that for hydrogen ($\alpha'/10^{-24}$ cm^3 for F = 0.38, H = 0.42, Cl = 2.28). On this basis, therefore, one would expect in the case of asymmetrically fluorinated ethanes that the relative reactivities at both sites of the molecule should be more nearly the same, which contradicts the present results and those of previous investigations (Table VII). Similar observations have also been made by Martens *et al.*[14] Of course, these arguments do not, in themselves, invalidate the conclusions of Johnston and Goldfinger with respect to the chlorinated methanes and ethanes, but merely indicate that an alternative explanation must be sought in the case of their fluorinated analogs.

The notion of electron withdrawal by the electronegative halogen with a concomitant weakening of the geminal C–H bond(s) as the *dominant* feature must also be questioned in the light of the fluorohydrocarbon results. If the latter were the case one could expect the geminal hydrogens in the fluorohydrocarbons to be more reactive than in their chlorinated analogs, based on the fact that fluorine is more electronegative than chlorine ($\chi_F = 3.98$, $\chi_{Cl} = 3.16$).[36] This, again, is contrary to experimental observation (Table VIII). However, the general trends outlined in Sec. V A for the fluoroethane series, are not inconsistent with a qualitative model of a concerted effect involving electron withdrawal from the geminal C–H bonds by the fluorine(s) in the molecule, and mutual repulsion between the fluorine(s) and the incoming chlorine atom. The existence of significant repulsion, as opposed to attractive dispersion forces, would explain, for example, why the activation energies for H abstraction in the fluoroethane series are generally higher than those for the corresponding chloroethanes.

E. Inductive and resonance effects

The interplay between inductive effects and resonance interactions in highly polar molecules has been discussed by Moore *et al.*[34] in their study of the relative reactivities in the sequential chlorination of 2,2-difluoropropane. Contrasting the relative reactivities (per H atom) in the liquid phase chlorination of 1-chloro-, 1,1-dichloro-, and 1,1,1-trichlorobutanes[31] where there is no adjacent strong inductive effect:

CH_3–CH_2–CH_2–CH_2Cl,
1.0 2.94 1.38 0.44

CH_3–CH_2–CH_2–$CHCl_2$,
1.0 1.95 0.53 0.16

CH_3–CH_2–CH_2– CCl_3
1.0 1.26 0.24 · · ·

with the relative reactivities in $(CH_3)_2CF_2$ and its chlorinated products:

CH_3–CF_2–CH_3,
1.0

CH_3–CF_2–CH_2Cl,
0.11 4.1

CH_3–CF_2–$CHCl_2$,
0.11 4.4

CH_3–CF_2–CCl_3.
0.12 · · ·

Moore *et al.*[34] postulated that when a polar group such as fluorine is already present, the resonance effect of geminal chlorine on the abstraction of hydrogen overshadows the incremental increase in inductive effect, resulting in a higher reactivity of hydrogen in the 1 position.

Martens *et al.*[14] used this concept of resonance stabilization of the incipient free radical by the mesomeric donating effect of the halogen substituent to show that it can account for the main point of attack in chloro- and fluoroethanes being on the more substituted side of the molecule

$$RCH_2\underline{X}| + Cl \rightarrow HCl + R\text{–}\dot{C}H\text{–}\underline{X}| \rightleftharpoons R\text{–}\overset{-}{C}H = \overset{+}{\underline{X}}|$$

even when R is a methyl group. The lower reactivity and possibly higher selectivity for H abstraction from the fluorinated ethanes compared with their chlorinated homologs can then be explained by the combined inductive and resonance effects, the bound fluorine atom being both a stronger inductive captor and a stronger mesomeric donor than the corresponding chlorine.

Our results conform with this scheme. Table IX lists the reactivities on a per available hydrogen basis for the fluoroethane series relative to our value[16] for C_2H_6 (Table VI) set equal to 1000, and indicates the contributing resonance and inductive effects. It is clear that the inductive effect which reduces the hydrogen reactivity increases with the number of fluorine substituents, both in the geminal and vicinal positions. This decrease in reactivity is counteracted by the resonance effect which enhances the reactivity on the same carbon atom. Thus the relative reactivity of any pair of compounds in Table IX with a resonance contribution is dictated mainly by the inductive effects, or the number of fluorines. This explains, for example, why the methylene hydrogen in CH_3CH_2F is about eight times more reactive than the methine hydrogen in CH_3CHF_2. As stated by Moore *et al.*[34] the resonance effect may "overshadow" the incremental increase in inductive effect, thus the reactivity of H in CH_2FCH_2F with two fluorines is 1.6 times higher than the methyl

TABLE IX. Relative reactivity (per H atom) at 298 K.[a]

		Inductive effect[b]		
Compound	Rate	Geminal	Vicinal	Resonance effect
CH_3CH_3	1000	...	...	...
$CH_3C\underline{H}_2F$	352	1	...	c
$CH_3C\underline{H}F_2$	46.4	2	...	c
CH_2FCH_2F	37.3	1	1	c
$C\underline{H}_3CH_2F$	24.9	...	1	...
$CH_2FC\underline{H}F_2$	2.63	2	1	c
$C\underline{H}_2FCHF_2$	1.28	1	2	c
CHF_2CHF_2	0.177	2	2	c
$C\underline{H}_3CHF_2$	0.149	...	2	...
$C\underline{H}_3CF_3$	8.97×10^{-4}	...	3	...

[a] Data relative to $k_{C_2H_6}/6$ from Ref. 16 and Table VI, normalized to 1000.

[b] Numbers indicate fluorine substituents.

[c] Indicates presence of effect.

hydrogen in $C\underline{H}_3CH_2F$. A slight aberration to the scheme is noted in the pairs $CH_3C\underline{H}F_2/CH_2FCH_2F$ and $CH_2FC\underline{H}F_2/C\underline{H}_2FCHF_2$, with two and three fluorine atoms, respectively. Since the inductive contribution falls off with separation one would expect the relative rates to be in the order $CH_2FCH_2F > CH_3C\underline{H}F_2$, and $C\underline{H}_2FCHF_2 > CH_2FC\underline{H}F_2$, while the reverse is observed. However, the differences in the rates are relatively small, and may reflect deviations in the respective A-factor ratios which depend on FID sensitivity corrections. In the absence of a resonance contribution, i.e., the abstraction of hydrogen from the methyl group in the series CH_3CH_3, CH_3CH_2F, CH_3CHF_2, CH_3CF_3 the reactivity is governed by inductive effects. For the two extreme cases, C_2H_6 with no inductive contribution, and CH_3CF_3 where there are three vicinal fluorines, the rates differ by more than six orders of magnitude.

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