

**COMPETITIVE PHOTOCHLORINATION OF THE FLUOROETHANES  
CH<sub>3</sub>CHF<sub>2</sub>, CH<sub>2</sub>FCH<sub>2</sub>F AND CHF<sub>2</sub>CHF<sub>2</sub>**T. YANO<sup>†</sup> and E. TSCHUIKOW-ROUX*Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4 (Canada)*

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**Summary**

The abstraction of hydrogen by photochemically generated ground state chlorine atoms from CH<sub>3</sub>CHF<sub>2</sub>, CH<sub>2</sub>FCH<sub>2</sub>F and CHF<sub>2</sub>CHF<sub>2</sub> has been investigated between 280 and 360 K using the competitive technique based on product analysis. Relative Arrhenius parameters are reported for the internal competition in CH<sub>3</sub>CHF<sub>2</sub> and the external competition for the pairs CH<sub>3</sub>CHF<sub>2</sub>-CH<sub>2</sub>FCH<sub>2</sub>F, CH<sub>3</sub>CHF<sub>2</sub>-CHF<sub>2</sub>CHF<sub>2</sub> and CH<sub>3</sub>CHF<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>. Absolute Arrhenius parameters are evaluated based on the recent direct determination of the rate coefficient for the reaction Cl + C<sub>2</sub>H<sub>6</sub> → C<sub>2</sub>H<sub>5</sub> + HCl by the low pressure discharge-flow-resonance fluorescence technique. The results are interpreted in terms of combined inductive effects and resonance stabilization of the incipient fluoroethyl radicals.

**1. Introduction**

The reaction kinetics of Cl(<sup>2</sup>P<sub>1/2</sub>) atoms with some chloro derivatives of C<sub>1</sub> and C<sub>2</sub> alkanes have recently received renewed attention [1 - 6], and this includes studies of competitive photochlorinations from this laboratory [7, 8]. In contrast, fewer kinetic investigations have been reported of the corresponding chlorine atom reactions with fluorohydrocarbons [9 - 12]. Nevertheless, a comparison of the reactivity trends for hydrogen atom abstraction by chlorine from chloro- and fluoro-substituted alkanes is of fundamental interest. The competitive photochlorination of C<sub>2</sub>H<sub>5</sub>F and CH<sub>3</sub>CHF<sub>2</sub> have been reported by Martens *et al.* [10] and Cadman *et al.* [11], who also obtained approximate data for hydrogen abstraction from 1,1,1-trifluoroethane. The reported rate parameters in this earlier work were not in particularly good agreement, even with respect to internal competition, as, for example, in the abstraction of primary and tertiary hydrogens in CH<sub>3</sub>CHF<sub>2</sub>. Most recently we have reported competitive chlorination rate constant data for several partially fluorinated methanes and ethanes, including CH<sub>3</sub>CHF<sub>2</sub> [12]. In this work, absolute Arrhenius parameters were

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based on the competitors  $C_2H_5Cl$  as a secondary, and  $CH_4$  as a primary standard. For the purpose of extended comparisons between the chlorination of fluoroethanes and the corresponding chloroethanes, some results on the chlorination of 1,1-difluoroethane and 1,1,2,2-tetrafluoroethane were also included, but no details were provided [12].

In this paper we present the original detailed re-examination of the internal competition in  $CH_3CHF_2$  and its respective competitive photochlorination with the symmetrical fluoroethanes  $CH_2FCH_2F$  and  $CHF_2CHF_2$ . Reported absolute rate parameters are based on the competition between  $CH_3CHF_2$  and ethane, the latter rate coefficient being known from direct kinetic measurements [13].

## 2. Experimental details

Details of the apparatus, light source and experimental procedure have been described previously [7]. Photolyses were carried out with excess fluorohydrocarbon(s) over  $Cl_2$  in a greaseless static system in the temperature range 280 - 360 K using light from a mercury lamp (Osram, HBO 500) after passing it through a Corning Glass combination filter which selects wavelengths around 415 nm (10.8%), 436 nm (18.2%) and 450 nm (10.8%) with an effective zero-percent transmittance below 406 nm. Reactant mixtures were prepared using a precision digital pressure gauge with a quartz Bourdon capsule (Texas Instruments model 145-01) in conjunction with expansion into a known volume and sequential condensation. The temperature of the reactor was controlled to within  $\pm 0.2^\circ C$  using a Lauda circulating bath, and dark reactions were ascertained to be absent.

Four systems were examined: the internal competition for  $\alpha$ - and  $\beta$ -hydrogen abstraction in  $CH_3CHF_2$  and the competition between the pairs  $CH_3CHF_2$ - $CH_2FCH_2F$ ,  $CH_3CHF_2$ - $CHF_2CHF_2$  and  $CH_3CHF_2$ - $C_2H_6$ , with  $C_2H_6$  serving as a primary standard. Competitor ratios were chosen to achieve comparable rates of hydrogen abstraction for a pair of reactants. The only carbon-containing products observed were the primary chlorination products  $CH_3CF_2Cl$  and  $CH_2ClCHF_2$  in the internal competition of  $CH_3CHF_2$ , and  $CH_3CF_2Cl$ ,  $CH_2FCHFCl$ ,  $CHF_2CF_2Cl$  and  $C_2H_5Cl$  in the other systems.

Quantitative product analysis was carried out by means of flame ionization gas chromatography (GC) with temperature programming (Hewlett-Packard, model 5830A), using a 3 m Poropak N column and helium as a carrier gas. Temperature programming was adjusted to give the optimum analytical conditions for the different pairs of compounds. Since, with the exception of  $CH_3CF_2Cl$  and  $C_2H_5Cl$ , authentic samples of the reaction products were not available, they were first confirmed in preliminary experiments using a coupled GC-mass spectroscopy (MS) instrument (computer-controlled Hewlett-Packard, model HP-5992A).

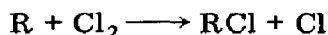
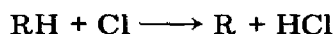
The reactants and some of the product chemicals were obtained commercially:  $Cl_2$ ,  $C_2H_6$  and  $C_2H_5Cl$  from Matheson;  $CH_3CHF_2$ ,  $CH_2FCH_2F$  and

CH<sub>3</sub>CF<sub>2</sub>Cl from ICN Pharmaceuticals, K & K Laboratories; CHF<sub>2</sub>CHF<sub>2</sub> from PCR Research Chemicals, Inc. All of the fluoroethanes were purified by preparative GC prior to their use. The final purity achieved was CH<sub>2</sub>FCH<sub>2</sub>F 99.99%, CHF<sub>2</sub>CHF<sub>2</sub> 99.99% and CH<sub>3</sub>CHF<sub>2</sub> 99.95%. The residual impurity of 0.05% CH<sub>2</sub>FCH<sub>2</sub>F in the CH<sub>3</sub>CHF<sub>2</sub> was tolerated. Research grade Cl<sub>2</sub> of stated purity 99.96% and C<sub>2</sub>H<sub>6</sub> (99.99%) were used without further purification.

### 3. Results

#### 3.1. Data reduction

In all cases other than the internal competition in CH<sub>3</sub>CHF<sub>2</sub>, the competing reactants were used in a large excess over chlorine (>25:1). As shown previously [7], under these conditions the long chain assumption is satisfied and chain termination is predominantly by radical combination. The light intensity and photolysis times were chosen to obtain sufficiently high primary product yields for accurate measurements but to be below the limit of detection of secondary chlorination products. Furthermore, since the abstraction of hydrogen by ground state chlorine atoms produces radicals which for all practical purposes are thermal, they can undergo neither unimolecular processes such as decomposition or rearrangement nor metathesis reactions, as can be shown on the basis of the kinetic data in the literature [9] or inferred from the product analysis. Under these conditions the observed photochlorination products are derived from the propagation steps



where R represents any of the possible fluoroethyl or ethyl radicals. For competitive photochlorination of RH with a reference compound R'H, the rate constant ratio in terms of the product yields is expressed conveniently in the form [12]

$$\frac{k}{k'} = \frac{[RCl][R'H]_0 F}{[R'Cl][RH]_0 F'} \quad (I)$$

where [RCl]/[R'Cl] is the measured product ratio, [R'H]<sub>0</sub>/[RH]<sub>0</sub> is known from the initial mixture composition based on pressure measurements, and *F* and *F'* are correction factors for higher conversion:

$$F = 1 + \frac{1}{2} \alpha + \frac{1}{3} \alpha^2 + \frac{1}{4} \alpha^3 + \dots \quad (II)$$

where  $\alpha \equiv [RCl]/[RH]_0$ , with an analogous expression existing for *F'*. The evaluation of the *F* is discussed later. Here, it may be noted that in the limit of very low conversion ( $\alpha \ll 1$ ), the *F* are effectively unity. Equation

(I) is exact, subject only to the validity of the long chain postulate. For the same conditions and internal competition the rate constant ratio is given rigorously by the product ratio directly:

$$\frac{k}{k'} = \frac{[\text{RCI}]}{[\text{R}'\text{Cl}]} \quad (\text{III})$$

### 3.2. Internal competition: chlorination of $\text{CH}_3\text{CHF}_2$

The abstraction of tertiary and primary hydrogen in  $\text{CH}_3\text{CHF}_2$  represents an internally competitive system



which yields the observed chlorination products  $\text{CH}_3\text{CF}_2\text{Cl}$  and  $\text{CH}_2\text{ClCHF}_2$ . Photochlorinations were carried out over the temperature range 10 - 85 °C at initial  $[\text{CH}_3\text{CHF}_2]_0/[\text{Cl}_2]_0$  of about 11. In a few cases this ratio was varied from a low value of 2.5 to a high value of 22, but this had no effect on the rate constant ratio, indicating that the underlying assumptions for the validity of eqn. (III) are justified. The results and experimental conditions are listed in Table 1 and the temperature dependence of the rate constant ratio is shown in Fig. 1. A least-squares analysis yields the relative rate parameters  $E_1 - E_1' = -2849 \pm 40 \text{ cal mol}^{-1}$  and  $A_1/A_1' = 0.896 \pm 0.052$  where the uncertainties represent one standard deviation ( $\pm 1\sigma$ ) and reflect

TABLE 1

Internal competition in the chlorination of  $\text{CH}_3\text{CHF}_2$

Run	P (Torr)			T (K)	$k_1/k_1'^a$
	$\text{CH}_3\text{CHF}_2$	$\text{Cl}_2$	$\text{C}_2\text{F}_6$		
1	4.0	0.37	0	283.4	145.9
2	4.0	0.38	0	283.4	140.5
3	4.0	0.38	0	283.4	143.5
4	3.9	0.38	0	293.0	120.1
5	2.5	0.98	0	293.2	115.2
6	2.3	0.38	0	293.2	118.4
7	8.2	0.38	0	293.5	115.7
8	2.9	0.26	17.7	293.9	118.2
9	4.0	0.38	0	312.9	87.1
10	3.9	0.37	0	332.8	66.8
11	2.9	0.26	19.0	333.6	67.3
12	4.0	0.37	0	351.4	53.8
13	4.0	0.38	0	351.4	53.8
14	3.9	0.38	0	351.6	51.8
15	3.9	0.38	0	356.6	49.4

<sup>a</sup> $k_1/k_1' = [\text{CH}_3\text{CF}_2\text{Cl}]/[\text{CH}_2\text{ClCHF}_2]$  (see eqn. (III)). The product sensitivities to the detector response were assumed to be equal.

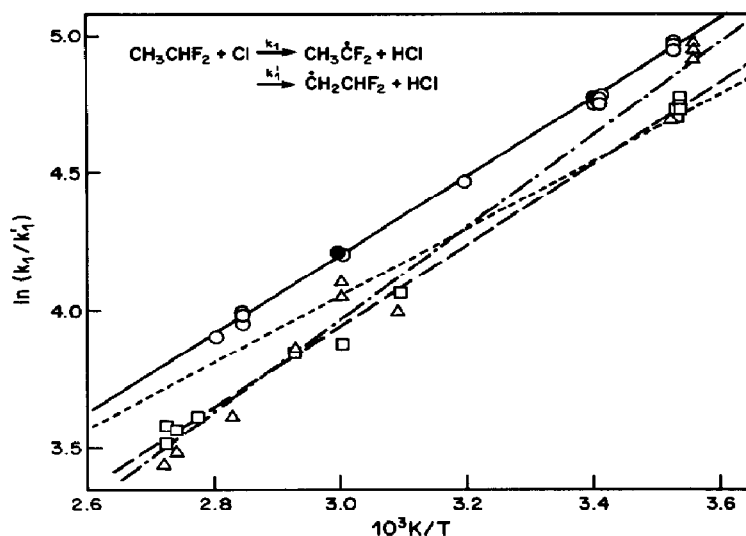


Fig. 1. Temperature dependence of the rate constant ratio  $k_1/k_1'$  for internal competition in  $\text{CH}_3\text{CHF}_2$ : — and  $\circ$ , from this work in the absence of  $\text{C}_2\text{F}_6$ ; — and  $\bullet$ , from this work in the presence of  $\text{C}_2\text{F}_6$ ; - - - and  $\Delta$ , from ref. 14 in the absence of  $\text{C}_2\text{F}_6$ ; - - - and  $\square$ , from ref. 14 in the presence of  $\text{C}_2\text{F}_6$ ; · · ·, from ref. 10.

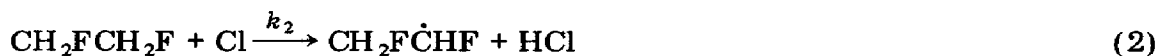
random errors only. Also shown in Fig. 1 are the internal competition data for  $\text{CH}_3\text{CHF}_2$  taken from the literature. Cadman *et al.* [11] reported the photochlorination of  $\text{CH}_3\text{CHF}_2$  over the temperature range 8 - 94 °C in the absence and presence of excess  $\text{C}_2\text{F}_6$ , and found an apparent inert gas effect. The initial  $[\text{CH}_3\text{CHF}_2]_0/[\text{Cl}_2]_0$  were varied from 8 to 63 with no  $\text{C}_2\text{F}_6$  and 6 to 16 in the presence of  $\text{C}_2\text{F}_6$ . The data points shown in Fig. 1 were taken not from ref. 11 but from A. W. Kirk's original Ph.D. Thesis [14] which lists the data points numerically. The  $\text{C}_2\text{F}_6$  appears to decrease the activation energy difference and increase the  $A$ -factor ratio for  $k_1/k_1'$ . However, no such effect was observed in the present study (runs 8 and 11, Table 1). While the original purpose of adding  $\text{C}_2\text{F}_6$  in A. W. Kirk's work was to provide an efficient quencher, it was subsequently used routinely since the results were found to be more reproducible [14]. This may be seen from Fig. 1 where the data in the absence of  $\text{C}_2\text{F}_6$  show a considerably larger scatter. It is likely that the difference in Kirk's data in the absence and presence of  $\text{C}_2\text{F}_6$  is a result of improved collection efficiency in the latter case; the reaction products were analysed after condensation at liquid air temperature [15].

Our result for the activation energy difference  $E_1 - E_1'$  is in excellent agreement with the value determined by Kirk in the presence of  $\text{C}_2\text{F}_6$ , the Arrhenius plots being almost parallel. The difference in the pre-exponential factor ratios, which depend on the relative detector sensitivities toward the photochlorination products, is not unreasonable, considering the differences in analytical procedures, although in the two studies the calibration factors for  $\text{CH}_3\text{CF}_2\text{Cl}$  and  $\text{CH}_2\text{ClCHF}_2$  were assumed to be the same.

Martens *et al.* [10] studied the photochlorination of  $\text{CH}_3\text{CHF}_2$  between  $-9$  and  $60^\circ\text{C}$  in a flow system at atmospheric pressure with helium as a diluent, at a total reagent pressure of about 80 Torr. The  $\text{CH}_3\text{CHF}_2:\text{Cl}_2$  ratio was not reported. Their Arrhenius plot for the internal competition is also shown in Fig. 1. In view of the relatively narrow temperature range of all three studies, the results of Martens *et al.* differ significantly from those reported in the present work or that by Cadman *et al.* [11].

### 3.3. Chlorination of $\text{CH}_3\text{CHF}_2$ and $\text{CH}_2\text{FCH}_2\text{F}$

Two  $\text{CH}_3\text{CHF}_2\text{-CH}_2\text{FCH}_2\text{F}$  mixtures (1:1 and 2:1) were photochlorinated between 15 and  $85^\circ\text{C}$  at a total pressure of about 10 Torr. The fluorohydrocarbon:chlorine ratio ranged from 25:1 to 39:1. Preliminary experiments had shown that the rate of the hydrogen abstraction in 1,2-difluoroethane



was comparable with the rate of abstraction of the methine hydrogen in  $\text{CH}_3\text{CHF}_2$ . Accordingly, photolysis times were chosen to give the products  $\text{CH}_2\text{FCHFCl}$  and  $\text{CH}_3\text{CF}_2\text{Cl}$ , while  $\text{CH}_2\text{ClCHF}_2$  was observed only as a trace product. Since an authentic sample of  $\text{CH}_2\text{FCHFCl}$  was not available, the latter was identified by means of GC-MS analysis. Subsequent GC product ratio determinations were corrected for the relative detector sensitivities assuming that the sensitivity ratio  $S(\text{CH}_3\text{CF}_2\text{Cl})/S(\text{CH}_2\text{FCHFCl})$  is roughly equal to the corresponding measured ratio  $S(\text{CH}_3\text{CHF}_2)/S(\text{CH}_2\text{FCH}_2\text{F}) = 1.096$ , for the reactants. The experimental conditions and the rate constant

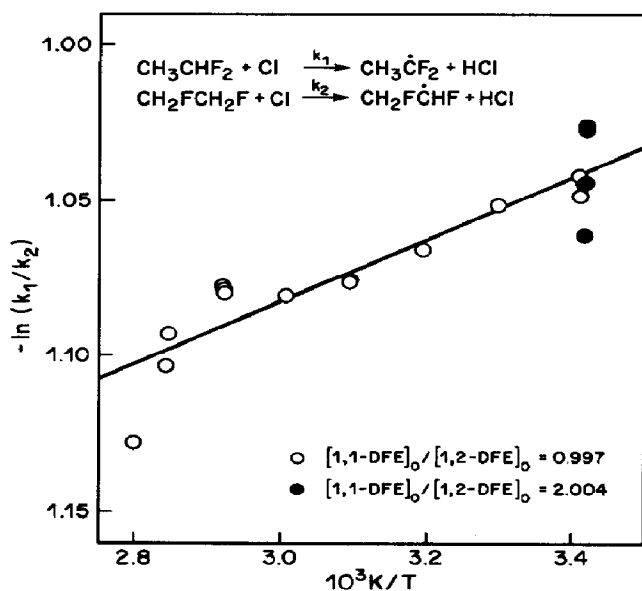


Fig. 2. Temperature dependence of the rate constant ratio  $k_1/k_2$  for hydrogen abstraction in  $\text{CH}_3\text{CHF}_2\text{-CH}_2\text{FCH}_2\text{F}$  mixtures.

ratios  $k_1/k_2$  obtained from eqn. (I) are listed in Table 2 and an Arrhenius plot is shown in Fig. 2. From a least-squares analysis we obtain  $E_1 - E_2 = -198 \pm 22 \text{ cal mol}^{-1}$ , and a statistical  $A$ -factor ratio  $A_1/A_2 = 0.251 \pm 0.009$ . The effect of adding excess  $C_2F_6$  was also examined but there was no apparent change in the rate constant ratio (runs 7, 15 and 16, Table 2).

TABLE 2

Chlorination of  $CH_3CHF_2$  and  $CH_2FCH_2F$ 

Run	P (Torr)			T (K)	$k_1/k_2^b$
	(RH + R'H) <sup>a</sup>	Cl <sub>2</sub>	C <sub>2</sub> F <sub>6</sub>		
1	10.1	0.29	0	292.7	0.3519
2	10.2	0.28	0	293.2	0.3526
3	10.1	0.27	0	293.2	0.3505
4	10.1	0.27	0	303.2	0.3494
5	10.2	0.28	0	313.0	0.3444
6	10.1	0.28	0	323.2	0.3410
7	10.3	0.28	30.3	323.2	0.3409
8	10.1	0.28	0	332.5	0.3393
9	9.4	0.24	0	342.1	0.3395
10	9.8	0.27	0	342.2	0.3399
11	10.2	0.28	0	342.6	0.3403
12	10.2	0.29	0	351.5	0.3352
13	9.0	0.23	0	352.0	0.3316
14	8.0	0.22	0	357.6	0.3236
15	9.6	0.30	58.7	292.5	0.3582
16	9.5	0.37	80.6	292.5	0.3580
17	10.2	0.36	0	292.6	0.3519
18	10.1	0.32	0	292.6	0.3419

<sup>a</sup>Runs 1-14:  $[RH]_0/[R'H]_0 = [CH_3CHF_2]_0/[CH_2FCH_2F]_0 = 0.997$ ; runs 15-18:  $[RH]_0/[R'H]_0 = 2.004$ .

<sup>b</sup>Based on the measured yields of the products  $CH_3CF_2Cl$  and  $CH_2FCHFCl$ .

### 3.4. Chlorination of $CHF_2CHF_2$ and $CH_3CHF_2$

Exploratory experiments showed that the rate coefficient for hydrogen abstraction from  $CHF_2CHF_2$



was much smaller than that for reaction (1a) and was comparable with that for reaction (1b). Accordingly, to avoid secondary chlorination of the reference product  $CH_3CF_2Cl$ , a very high ratio of  $CHF_2CHF_2$  to  $CH_3CHF_2$  was used. Nevertheless, in this instance, the following correction for higher conversion was applied. To facilitate the evaluation of the  $F$  in eqn. (I) a small amount (2.2%) of  $C_2F_6$  was added to the reaction mixture to provide an internal reference. Thus from the known initial  $[CHF_2CHF_2]_0/[C_2F_6]_0$  and  $[CH_3CHF_2]_0/[C_2F_6]_0$  before photolysis, and the measured  $[CHF_2CF_2Cl]/[C_2F_6]_0$  and  $[CH_3CF_2Cl]/[C_2F_6]_0$  after photolysis, the values of  $\alpha$  and

$\alpha'$  in eqn. (II) and hence  $F$  and  $F'$  could be determined. In the absence of an authentic sample of  $\text{CHF}_2\text{CF}_2\text{Cl}$  the ratio of the relative sensitivities to the flame ionization detector (FID) response for  $\text{CHF}_2\text{CF}_2\text{Cl}$  and  $\text{CH}_3\text{CF}_2\text{Cl}$  was again assumed to be equal to the corresponding ratio for  $\text{CHF}_2\text{CHF}_2$  and  $\text{CH}_3\text{CHF}_2$  ( $S(\text{CHF}_2\text{CHF}_2)/S(\text{CH}_3\text{CHF}_2) = 0.5690$ ). However, no sensitivity corrections were applied in the evaluation of the  $F$  since, for relatively low conversions, these factors are close to unity to a first approximation. Pertinent data and results are summarized in Table 3 and the temperature dependence of the rate constant ratio  $k_3/k_1$  is shown in Fig. 3, yielding the relative rate parameters  $E_3 - E_1 = 2937 \pm 40 \text{ cal mol}^{-1}$  and  $A_3/A_1 = 1.28 \pm 0.09$ .

TABLE 3

Chlorination of  $\text{CHF}_2\text{CHF}_2$  and  $\text{CH}_3\text{CHF}_2$ 

$P$ (Torr)		$T$ (K)	$10^2 \times k_3/k_1^b$
Fluoroethanes <sup>a</sup>	$\text{Cl}_2$		
20.5	0.13	282.7	0.6979
21.1	0.14	293.3	0.8189
20.6	0.14	313.1	1.150
20.5	0.14	332.9	1.476
20.6	0.15	352.3	1.941
20.6	0.14	352.3	1.937
20.4	0.14	357.0	2.062

<sup>a</sup>Mixture composition:  $[\text{CHF}_2\text{CHF}_2]_0/[\text{CH}_3\text{CHF}_2]_0 = 257.1$  with 2.2%  $\text{C}_2\text{F}_6$  as a reference compound.

<sup>b</sup>Based on the measured yields of the products  $\text{CHF}_2\text{CF}_2\text{Cl}$  and  $\text{CH}_3\text{CF}_2\text{Cl}$ .

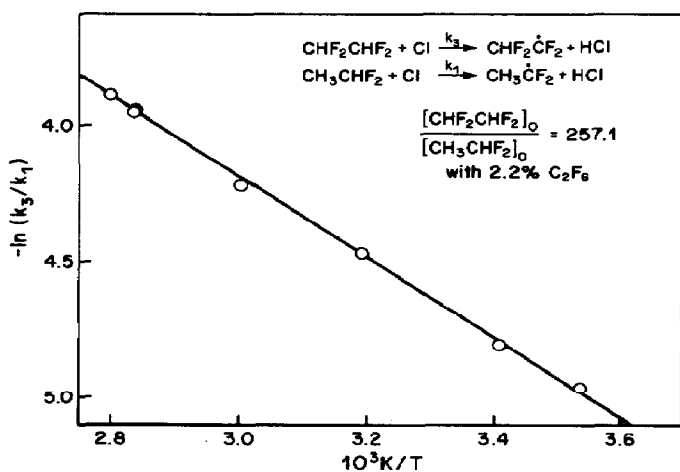


Fig. 3. Temperature dependence of the rate constant ratio  $k_3/k_1$  for hydrogen abstraction from  $\text{CHF}_2\text{CHF}_2$  and  $\text{CH}_3\text{CHF}_2$ .



### 3.5. Chlorination of $\text{CH}_3\text{CHF}_2$ against $\text{C}_2\text{H}_6$ and absolute rate parameters

In order to obtain absolute values of the rate parameters for the fluoroethanes,  $\text{CH}_3\text{CHF}_2$  was photochlorinated against  $\text{C}_2\text{H}_6$  as a primary standard. The latter reaction has been investigated on many occasions, both in competitive systems [5, 16] and by direct kinetic spectroscopy methods [2, 5, 6, 13], and the temperature dependence of the rate coefficient is believed to be reasonably well established [13]. Since over the temperature range of this investigation the rate constant for hydrogen abstraction from ethane



is some two orders of magnitude higher than for reaction (1a),  $\text{CH}_3\text{CHF}_2$  was used in about a 100-fold excess. Again, about 2%  $\text{C}_2\text{F}_6$  was added as an internal standard. The experimental conditions and rate constant ratios are listed in Table 4. In this case the relative detector sensitivities of the products were determined and applied:  $S(\text{CH}_3\text{CF}_2\text{Cl})/S(\text{C}_2\text{H}_5\text{Cl}) = 0.985$ . An Arrhenius plot is shown in Fig. 4, yielding an activation energy difference  $E_1 - E_4 = 1720 \pm 40 \text{ cal mol}^{-1}$  and an A-factor ratio of  $A_1/A_4 = 0.0835 \pm 0.006$ .

The results of the respective competitive photochlorinations are listed in Table 5. The absolute rate parameters based on the rate constant value

$$k_4 (\text{cm}^3 \text{s}^{-1}) = (9.01 \pm 0.48) \times 10^{-11} \exp\left(-\frac{264 \pm 30}{RT}\right)$$

(where  $R$  is in calories per kelvin per mole) reported recently by Lewis *et al.* [13] using the low pressure discharge-flow-resonance fluorescence (DF-RF) technique are given in Table 6.

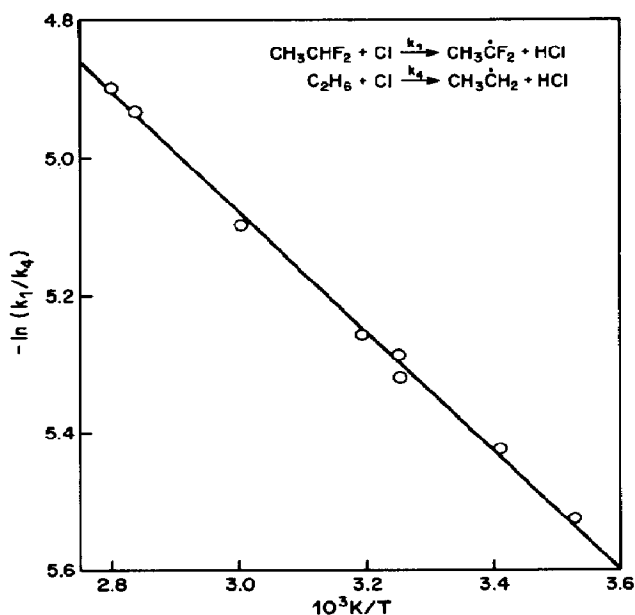


Fig. 4. Arrhenius plot of the rate constant ratio  $k_1/k_4$  for competitive hydrogen abstraction by chlorine atoms in  $\text{CH}_3\text{CHF}_2$ - $\text{C}_2\text{H}_6$  mixtures.

TABLE 4  
Competitive chlorination of  $\text{CH}_3\text{CHF}_2$  and  $\text{C}_2\text{H}_6$

$P$ (Torr)		$\text{Cl}_2$	$T$ (K)	$10^2 \times k_1/k_4^b$
$\text{C}_2$ compounds <sup>a</sup>				
20.5		0.11	283.4	0.3974
21.8		0.14	293.3	0.4405
21.9		0.14	307.4	0.4890
21.9		0.23	307.7	0.5059
22.5		0.14	313.1	0.5207
21.7		0.14	332.9	0.6099
22.3		0.13	352.3	0.7214
21.7		0.14	357.1	0.7475

<sup>a</sup>Mixture composition:  $[\text{CH}_3\text{CHF}_2]_0/[\text{C}_2\text{H}_6]_0 = 109.0$  with 2.2%  $\text{C}_2\text{F}_6$  as an additive for internal reference.

<sup>b</sup>Based on the measured yields of the products  $\text{CH}_3\text{CF}_2\text{Cl}$  and  $\text{C}_2\text{H}_5\text{Cl}$ .

TABLE 5  
Relative rate parameters for hydrogen abstraction by chlorine atoms<sup>a</sup>

Reactant $i$	Reactant $j$	$A_i/A_j^b$	$E_i - E_j$ (cal mol <sup>-1</sup> )	Reference
$\text{CH}_3\text{CHF}_2$	$\text{CH}_3\text{CHF}_2$	$0.896 \pm 0.052$	$-2849 \pm 40$	This work
		$0.631 \pm 0.03$	$-2917 \pm 31$	14 <sup>c</sup>
		$0.340 \pm 0.06$	$-3339 \pm 115$	14 <sup>d</sup>
		$1.48 \pm 0.03$	$-2425 \pm 15$	10
$\text{CH}_3\text{CHF}_2$	$\text{CH}_2\text{FCH}_2\text{F}$	$0.251 \pm 0.009^e$	$-198 \pm 22$	This work
$\text{CHF}_2\text{CHF}_2$	$\text{CH}_3\text{CHF}_2$	$1.282 \pm 0.09^f$	$2937 \pm 40$	This work
$\text{CH}_3\text{CHF}_2$	$\text{C}_2\text{H}_6$	$0.0835 \pm 0.006^g$	$1720 \pm 40$	This work

<sup>a</sup>Stated uncertainty limits are  $\pm 1\sigma$ .

<sup>b</sup>A-factor ratio refers to total hydrogen abstraction of a given type.

<sup>c</sup>From ref. 14, in the presence of  $\text{C}_2\text{F}_6$  as an inert additive.

<sup>d</sup>From ref. 14, in the absence of  $\text{C}_2\text{F}_6$ .

<sup>e</sup>Corrected for relative detector sensitivities assuming  $S(\text{CH}_3\text{CF}_2\text{Cl})/S(\text{CH}_2\text{FCH}_2\text{Cl})$  is equal to  $S(\text{CH}_3\text{CHF}_2)/S(\text{CH}_2\text{FCH}_2\text{F}) = 1.097$ .

<sup>f</sup>Corrected for relative detector sensitivities assuming  $S(\text{CHF}_2\text{CF}_2\text{Cl})/S(\text{CH}_3\text{CF}_2\text{Cl})$  is equal to  $S(\text{CHF}_2\text{CHF}_2)/S(\text{CH}_3\text{CHF}_2) = 0.569$ .

<sup>g</sup>Corrected for relative detector sensitivities:  $S(\text{CH}_3\text{CF}_2\text{Cl})/S(\text{C}_2\text{H}_5\text{Cl}) = 0.985$ .

#### 4. Discussion

The results in Table 6 confirm that the reactivity of hydrogen towards chlorine atom attack is strongly diminished by fluorine substitution. Within the fluoroethane series the different reactivities are governed primarily by differences in activation energies, which, in turn, reflect the number and position

TABLE 6

Absolute rate parameters for hydrogen abstraction by chlorine atoms from fluorinated ethanes<sup>a, b</sup>

Reactant	$A^c$ ( $\times 10^{-11}$ $\text{cm}^3 \text{s}^{-1}$ )	$E$ (cal $\text{mol}^{-1}$ )	$k_{298}$ ( $\text{cm}^3$ $\text{s}^{-1}$ )	$k_{298}/n$ ( $\text{cm}^3$ $\text{s}^{-1}$ )	Reference
$\text{C}_2\text{H}_6$	$9.01 \pm 0.048$	$264 \pm 30$	$5.77 \times 10^{-11}$	$0.962 \times 10^{-11}$	13
$\text{CH}_3\text{CHF}_2$	$0.752 \pm 0.067$	$1984 \pm 50$	$2.64 \times 10^{-13}$	$2.64 \times 10^{-13}$	This work
$\text{CH}_2\text{CHF}_2$	$0.840 \pm 0.090$	$4833 \pm 64$	$2.40 \times 10^{-15}$	$0.80 \times 10^{-15}$	This work
$\text{CH}_2\text{FCH}_2\text{F}$	$2.997 \pm 0.289$	$2182 \pm 55$	$7.53 \times 10^{-13}$	$1.88 \times 10^{-13}$	This work
$\text{CHF}_2\text{CHF}_2$	$0.964 \pm 0.110$	$4921 \pm 64$	$2.37 \times 10^{-15}$	$1.19 \times 10^{-15}$	This work

<sup>a</sup>Based on the reference reaction  $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{HCl} + \text{C}_2\text{H}_5$  ( $k_4$ ) [13].

<sup>b</sup>Stated uncertainties in Arrhenius parameters allow for error limits of the reference reaction.

<sup>c</sup>Statistical  $A$  factors.

<sup>d</sup>Rate constant per available hydrogen of a given kind.

of the fluorine substituents. The following observations can be made. (a) For the asymmetric  $\text{CH}_3\text{CHF}_2$  the rate of abstraction of the methine hydrogen, while being 36 times slower than the normalized rate of hydrogen abstraction in ethane, is about 330 times faster than the abstraction of hydrogen from the methyl group in 1,1-difluoroethane. (b) The activation energy increases with progressive fluorine substitution: the abstraction of tertiary hydrogen in  $\text{CHF}_2\text{CHF}_2$  is about 200 times slower than from the  $\text{CHF}_2$  group in  $\text{CH}_3\text{CHF}_2$ . (c) A comparison between the structural isomers shows an apparent compensating effect; thus the reactivity of the secondary hydrogen in  $\text{CH}_2\text{FCH}_2\text{F}$  is almost the same as that of the tertiary hydrogen in  $\text{CH}_3\text{CHF}_2$ .

Factors controlling the reactivity of alkyl halides towards halogenation or other forms of radical attack have been discussed by Tedder [17] and Tedder *et al.* [18]:



Considerations pertinent to the present discussion include (a) the strength of the R—H bond, (b) the repulsion between the incipient radical R and the forming HCl molecule and (c) the interaction between the incoming chlorine atom and the molecule RH. It is clear that (b) and (c) relate to properties of the transition state. A theoretical examination of the potential energy surface in terms of such semiempirical treatments as the London–Eyring–Polanyi–Sato (LEPS) [19, 20], the bond energy–bond order (BEBO) [20, 21] or the more recent bond strength–bond length (BSBL) [22, 23] formulations, or the Zavitsas [24] method, is not attempted here, since hydrogen atom abstraction by chlorine atoms from partially chlorinated methanes [20, 23–25] and ethanes [20, 25] presents a notable exception to these otherwise reasonably successful treatments. The reactivity trends

in the fluoroethane series [10 - 12] qualitatively parallel those in the chloroethanes [3, 4, 7, 8, 26]. Thus a failure of the above theoretical formulations would not be unanticipated. Moreover, an adequate thermochemical data base of measured C—H bond dissociation energies or heats of formation of haloethyl radicals is not available in either case [27] to permit a quantitative evaluation.

The reactivity trends shown in Table 6 are best discussed in terms of inductive and resonance interactions. Moore *et al.* [28] have summarized these opposing effects previously demonstrated by Tedder and coworkers [29 - 31] for end-substituted chloro- and fluoro- butanes and pentanes. Thus, the inductive effects of the halogens fluorine and chlorine tend to reduce the reactivity of hydrogens in their vicinity, these effects decreasing rapidly with increasing separation, while the resonance effects of the bound halogens increase the reactivity of the hydrogens on the same carbon atom. In the sequential chlorination of 1,1-difluoropropane, Moore *et al.* [28] further showed that when polar substituents such as fluorine are already present, the resonance effect of the geminal chlorine on the abstraction of hydrogen overshadows the incremental increase in the inductive effect, resulting in a successively higher hydrogen reactivity in the 1-position of the monochlorination and dichlorination products. The enhanced resonance stabilization of the incipient free radical by a strong captor group has also been discussed by Martens *et al.* [10] and the combined inductive and mesomeric donating effects of the halogen substituents have been invoked to explain their observed reactivity trends in the chlorination of  $C_2H_5F$ ,  $CH_3CHF_2$  and  $CH_3CHFCl$  [10]. Similar qualitative considerations apply to the present results. The low reactivity of the methine hydrogen in  $CH_3CHF_2$  relative to  $C_2H_6$  is indicative of the dominance of inductive effects, offset in part by resonance stabilization. The much lower reactivity of the primary hydrogen in  $CH_3CHF_2$  reflects the absence of a resonance contribution in the methyl group, the reactivity being influenced entirely by inductive effects from the vicinal  $CHF_2$  group. In the case of the symmetrical  $CH_2FCH_2F$  the reactivity is governed by inductive effects from one geminal and one vicinal fluorine substituent plus a compensating resonance contribution. Since the inductive effect decreases with separation one would expect the relative rates (per hydrogen atom) to be  $k(CH_2FCH_2F)/k(CH_3CH_2F_2) > 1$ . The observed value is 0.71, and may reflect the uncertainties in the  $A$  factors which depend on the relative FID sensitivity corrections. The reactivity in  $CHF_2CHF_2$  is roughly the same as that for the methyl hydrogen in  $CH_3CHF_2$ . This too can be interpreted in terms of the combined effects: the enhancement in the reactivity by resonance stabilization in  $CHF_2CHF_2$  is roughly offset by the additional inductive effect from the two geminal fluorine substituents, the vicinal group in the two molecules being the same.

In conclusion we note that the activation energies determined here with  $C_2H_6$  [13] used as a standard are in excellent agreement with those reported by us previously [12] with  $C_2H_5Cl$  [32] as secondary and  $CH_4$  [33]

as primary standards, and provide evidence for the internal consistency of the data and the accurate assessment of the chosen reference reactions for which rate parameters were determined independently by the direct DF-RF technique.

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### References

- 1 M. A. A. Clyne and R. F. Walker, *J. Chem. Soc., Faraday Trans. I*, **69** (1973) 1547.
- 2 R. G. Manning and M. J. Kurylo, *J. Phys. Chem.*, **81** (1977) 291.
- 3 P. H. Wine, D. H. Semmes and R. H. Ravishankara, *Chem. Phys. Lett.*, **90** (1982) 128.
- 4 P. H. Wine and D. H. Semmes, *J. Phys. Chem.*, **87** (1983) 3572.
- 5 R. T. Watson, *J. Phys. Chem. Ref. Data*, **6** (1977) 871.
- 6 Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling, *Evaluation No. 6, JPL Publication 83-62*, Jet Propulsion Laboratory, Pasadena, CA, 1983.
- 7 E. Tschuikow-Roux, T. Yano and J. Niedzielski, *J. Phys. Chem.*, **88** (1984) 1408.
- 8 E. Tschuikow-Roux, J. Niedzielski and F. Faraji, *Can. J. Chem.*, **63** (1985) 1093.
- 9 J. A. Kerr and S. J. Moss (eds.), *CRC Handbook of Bimolecular and Termolecular Gas Reactions*, Vol. I, CRC Press, Boca Raton, FL, 1981.
- 10 G. J. Martens, M. Godfroid, J. Delvaux and J. Verbeyst, *Int. J. Chem. Kinet.*, **8** (1976) 153.
- 11 P. Cadman, A. W. Kirk and A. F. Trotman-Dickenson, *J. Chem. Soc., Faraday Trans. I*, **72** (1976) 1027.
- 12 E. Tschuikow-Roux, T. Yano and J. Niedzielski, *J. Chem. Phys.*, **82** (1985) 65.
- 13 R. S. Lewis, S. P. Sander, S. Wagner and R. T. Watson, *J. Phys. Chem.*, **84** (1980) 2009.
- 14 A. W. Kirk, *Ph.D. Thesis*, University of Wales, 1968.
- 15 A. W. Kirk, private communication, 1984.
- 16 G. C. Fettis and J. H. Knox, in G. Porter (ed.), *Progress in Reaction Kinetics*, Vol. 2, Pergamon and Macmillan, New York, 1964, Chapter 1.
- 17 J. M. Tedder, *Quart. Rev. (London)*, **14** (1960) 336.
- 18 D. C. Nonhebel, J. M. Tedder and J. C. Walton, *Radicals*, Cambridge University Press, 1979, Chapter 8.
- 19 S. Sato, *J. Chem. Phys.*, **23** (1955) 2465.
- 20 H. S. Johnston, *Gas Phase Reaction Rate Theory*, Ronald, New York, 1966.
- 21 H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85** (1963) 2544.
- 22 T. Bérces and J. Dombi, *Int. J. Chem. Kinet.*, **12** (1980) 123.
- 23 T. Bérces and J. Dombi, *Int. J. Chem. Kinet.*, **12** (1980) 183.
- 24 A. A. Zavitsas and A. A. Melikian, *J. Am. Chem. Soc.*, **97** (1975) 2757.
- 25 H. S. Johnston and P. Goldfinger, *J. Chem. Phys.*, **37** (1962) 700.
- 26 C. Cillien, P. Goldfinger, G. Huybrechts and G. Martens, *Trans. Faraday Soc.*, **63** (1967) 1631.
- 27 D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.*, **33** (1982) 493.
- 28 L. O. Moore, C. E. Rectenwald and J. W. Clark, *Int. J. Chem. Kinet.*, **4** (1972) 331.
- 29 P. S. Fredricks and J. M. Tedder, *Chem. Ind.*, (1959) 490.
- 30 P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, (1960) 144.
- 31 I. Galiba, J. M. Tedder and R. A. Watson, *J. Chem. Soc.*, (1964) 1321.
- 32 J. Niedzielski, E. Tschuikow-Roux and T. Yano, *Int. J. Chem. Kinet.*, **16** (1984) 621.
- 33 J. F. Keyser, *J. Chem. Phys.*, **69** (1978) 214.