significantly from data for ordinary ion exchange) and yield reasonable values for intraparticle diffusivities. However, additional work is necessary to understand the effects of various co-ions on the measured diffusivities, as well as to uncover a model suitable for the case of low solution ionic capacity ($CV < \overline{CV}$).

Notation

C, mequiv/ml	Initial solution concentration
$\bar{C}$, mequiv/ml	Concentrations of fixed ionic groups in the solid exchanger
D_i, cm^2/sec	Solution phase diffusion coefficient for species i
$\bar{D}_i$, cm^2/sec	Intraparticle diffusion coefficient for species i
F, coulombs/mole	Faraday's constant
$F(t)$	Fractional attainment of equilibrium during neutralization
$G(t)$	Fractional exhaustion of resin during ordinary exchange with infinite solution boundary condition
r_0, cm	Radius of exchanger particle
R, ergs/mole °K	Gas constant
t, sec	Time
t_0, sec	Time for complete reaction
T, °K	Absolute temperature
u_i, cm^2/sec v	Mobility of species i
V, ml	Solution volume
$\bar{V}$, ml	Resin volume
τ	Dimensionless time

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The Photolysis of Fluoroacetone and the Elimination of Hydrogen Fluoride from "Hot" Fluoroethanes[1]

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Fluoroacetone was photolyzed in the region of 3130 A, and the rates of collisional stabilization *vs.* HF elimination of the "hot" fluoroethanes $C_2H_5F^*$ and $C_2H_4F_2^*$ produced in the system were examined as functions of the temperature and the pressure. The classical Rice–Ramsperger–Kassel theory of unimolecular reactions is shown to give a quantitative description of the decomposition of the "hot" molecules, as was demonstrated recently by Benson and Haugen[2] for $C_2H_4F_2^*$. The reduction in the number of effective oscillators in $C_2H_5F^*$, as opposed to $C_2H_4F_2^*$, results in the predicted enhancement of the rate of HF elimination from $C_2H_5F^*$. The values of the activation energies for H atom abstraction from the ketone are 4.6 and 6.7 kcal mole^{-1} for CH_3 and CH_2F radicals, respectively.

Introduction

There has been much recent interest in the elimination of HF from vibrationally excited fluoroethanes, formed by methyl radical recombination,[3-6] and the observed rates have been correlated with the decreasing number of effective oscillators in the molecules with decreasing fluorine atom content.[2] On this basis $C_2H_5F^*$ should show the greatest rate of HF elimination for a given set of experimental conditions.[2] This

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[1] This work was supported by a grant from the National Science Foundation.

[2] S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1965).

[3] G. O. Pritchard, M. Venugopalan, and T. F. Graham, *ibid.*, **68**, 1786 (1964).

work describes experiments with this "hot" molecule and also with $CH_2FCH_2F^*$, which is formed in the system.

Experimental Section

The apparatus and procedure have been described.[8] The ketone was obtained from City Chemical Corp. and it was purified by vpc. Its mass spectrum is given in Table I. The base peak is due to CH_3CO^+, as is the case in the mass spectrum of CH_3COCF_3.[7] A similar observation[8] was made with $C_2H_5COC_3F_7$, although the base peak was $C_2H_5^+$ rather than $C_2H_5CO^+$. The photolysis pattern of unsymmetrical fluoro ketones shows the same preferred dissociative mode; *e.g.*

Table I: Mass Spectrum of Fluoroacetone

m/e	Probable positive ion	Relative abundance[a]
12	C	2.0
13	CH	4.3
14	CH_2	15.4
15	CH_3	46.8
25	C_2H	1.9
26	C_2H_2	5.8
27	C_2H_3	10.7
28	CO	2.3
29	CHO	5.8
31	CF	3.4
32	CHF	2.3
33	CH_2F	21.6
37	C_3H	2.0
38	C_3H_2	1.7
39	C_3H_3	1.6
40	C_2O	1.2
41	C_2HO	1.5
42	C_2H_2O	8.3
43	C_2H_3O	100.0
45	C_2H_2F	1.9
47	C_2H_4F	2.0
58	C_3H_3F	2.0
61	C_2H_2FO	5.7
76	C_3H_5FO	6.1

[a] m/e less than 1% of the 43 ion peak have been omitted; no isotope corrections have been made and isotope peaks have been omitted.

$$CH_3COCF_3 + h\nu \longrightarrow CH_3CO + CF_3$$

and

$$C_2H_5COC_2F_5 + h\nu \longrightarrow C_2H_5CO + C_2F_5$$

have been established as the primary acts in the respective photodecompositions at 3130 A.[9,10] It is therefore probable that

$$CH_2FCOCH_3 + h\nu \longrightarrow CH_2F + COCH_3 \qquad (1)$$

is the primary photolytic decomposition step at 3130 A in the photolysis of fluoroacetone.

Some quantum yield data are reported; in these experiments the 3130-A line was isolated with an interference filter supplied by Farrand Optical Co.; the peak wavelength was at 3135 A, with a half band width of 90 A. The incident intensity was 9.4×10^{13} quanta cc^{-1} sec^{-1}. The extinction coefficient of the ketone at 3130 A is 4.9 l. $mole^{-1}$ cm^{-1}, where $\log (I_0/I) = \epsilon cl$.

CO and CH_4 were collected at −210° and analyzed by vpc on an activated charcoal column. C_2H_6, C_2H_4, CH_3F, C_2H_3F, and C_2H_5F were collected at −145° and analyzed on a 2-m 3% squalane-on-alumina column. The $C_2H_4F_2$, plus some ketone, was collected at −80° and analyzed on a short (0.5-m) 3% squalane-on-alumina column, on which the ketone was retained. The separation was conducted in this manner to reduce the retention time for the $C_2H_4F_2$. The columns were calibrated with pure samples of each of the compounds. No search was made for any of the high-boiling products.

A series of experiments at 382°K was conducted with various added pressures of perfluorocyclohexane. This contained a very small impurity which showed up as a peak similar in area and very close to the C_2H_5F peak on the chromatograms. To remove any ambiguity in our determination of C_2H_5F, some further experiments were carried out with n-C_6F_{14}, which did not show any evidence of such an impurity.

Results

Quantum Yields and H Atom Abstractions. The data on 14 experiments over the temperature range 329-585°K are reported in Table II. In these experiments the ketone pressure varied between 4 and 7 cm, although most of the runs were carried at 6 ± 0.2 cm. Those marked with a Φ indicate that quantum yield determinations were made and these are given in Table III. In some quantum yield experiments carried out at room temperature very little CO and no C_2H_6 was obtained, although some ethylene and fluorine-containing products were formed. At 56° the

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(4) G. O. Pritchard and J. T. Bryant, *J. Phys. Chem.*, **69**, 1085 (1965); **70**, 1441 (1966).

(5) R. D. Giles and E. Whittle, *Trans. Faraday Soc.*, **61**, 1425 (1965).

(6) W. G. Alcock and E. Whittle, *ibid.*, **61**, 244 (1965).

(7) J. R. Majer, *Advan. Fluorine Chem.*, **2**, 55 (1961).

(8) G. O. Pritchard and R. L. Thommarson, *J. Phys. Chem.*, **69**, 1001 (1965).

(9) E. A. Dawidowicz and C. R. Patrick, *J. Chem. Soc.*, 4250 (1964).

(10) R. L. Thommarson and G. O. Pritchard, *J. Phys. Chem.*, **70**, 2307 (1966).

Table II: Data on CH_2FCOCH_3 Photolysis[a]

				[Product] × 10^6, moles							
Run	Temp, °K	Time, sec	[Ketone] × 10^6, moles cc^{-1}	CO	CH_4	C_2H_6	C_2H_4	CH_3F	C_2H_3F	C_2H_5F	$C_2H_4F_2$
1Φ	329	7200	2.90	1.23	1.09	0.008	0.138	0.361	0.343	0.024	0.284
2	362	1800	2.65	15.5	11.3	0.158	1.66	1.04	1.85	0.389	1.48
3Φ	382	7200	1.68	10.6	7.30	0.150	1.29	0.656	1.12	...	...
4Φ	406	7200	2.32	13.6	9.36	0.145	1.04	1.49	1.12	0.223	0.838
5	417	1500	2.26	28.0	17.0	0.390	2.71	1.73	2.28	0.497	1.82
6Φ	420	5400	2.57	14.5	8.46	0.186	1.28	1.31	0.930	0.218	...
7	450	1200	2.00	23.1	13.3	0.433	2.49	1.61	2.10	0.336	1.37
8Φ	464	7200	2.01	15.2	11.2	0.092	0.651	2.57	0.937	0.118	0.555
9	480	900	1.97	18.0	10.8	0.293	1.82	1.66	1.42	0.252	0.935
10	505	900	1.81	18.9	12.3	0.283	1.69	2.44	1.67	0.192	0.802
11Φ	525	5400	1.87	15.5	11.9	0.066	0.407	3.11	0.620	0.062	...
12Φ	552	5400	1.69	12.7	9.29	0.044	0.312	4.63	0.474	0.045	0.111
13	571	600	1.66	13.4	9.66	0.094	0.699	3.15	0.880	0.096	0.262
14Φ	585	3600	1.65	9.73	7.88	0.025	0.225	4.61	2.79	...	...

[a] The mass balance ratio = $(^1/_2CH_4 + C_2H_6 + C_2H_4 + {}^1/_2CH_3F + C_2H_3F + C_2H_5F + C_2H_4F_2)/CO = 0.63 \pm 0.3$, except for run 1 where it is 1.24, owing to the nondissociative fate of CH_3CO below 100°; see text.

Table III: Quantum Yields of the Products of the Photolysis of CH_2FCOCH_3 at 3130 A

Temp, °K	CO	CH_4	C_2H_6	C_2H_4	CH_3F	C_2H_3F	C_2H_5F	$C_2H_4F_2$
329	0.065	0.057	0.0004	0.007	0.019	0.002	0.001	0.001
382	1.04	0.711	0.015	0.125	0.064	0.109	...	...
406	0.995	0.684	0.010	0.096	0.109	0.082	0.016	0.061
420	1.08	0.629	0.013	0.095	0.097	0.069	0.021	...
464	0.939	0.690	0.006	0.040	0.158	0.058	0.007	0.034
525	1.21	0.925	0.005	0.031	0.243	0.048	0.004	...
552	0.899	0.659	0.003	0.022	0.328	0.034	0.003	0.008
585	0.948	0.767	0.002	0.022	0.449	0.027	...	...

ethane quantum yield was approximately 4×10^{-4}, although $\Phi_{CO} \cong \Phi_{CH_4}$ (Table III). This substantiates that reaction 1 represents the primary split and that below 100° ($\Phi_{CO} \approx 1$ at 109°) the acetyl radicals play a role in the mechanism. Consequently hydrogen abstraction data on the reactions

$$CH_3 + CH_2FCOCH_3 \longrightarrow CH_4 + CHFCOCH_3 \text{ or } CH_2FCOCH_2 \quad (2)$$

and

$$CH_2F + CH_2FCOCH_3 \longrightarrow CH_3F + CHFCOCH_3 \text{ or } CH_2FCOCH_2 \quad (3)$$

vs. radical recombination data

$$2CH_3 \longrightarrow C_2H_6 \quad (4)$$

and

$$2CH_2F \longrightarrow C_2H_4F_2 \text{ or } C_2H_3F + HF \quad (5)$$

will be complicated by the reactions

$$CH_3 + CH_3CO \longrightarrow CH_4 + CH_2CO$$

$$CH_2F + CH_3CO \longrightarrow CH_3F + CH_2CO$$

That this is so is evident in the Arrhenius plots given in Figure 1. Least-squares lines of the functions (above 100°)

$$k_2/k_4^{1/2} = R_{CH_4}/R_{C_2H_6}{}^{1/2}[\text{ket}]$$

and

$$k_3/k_5^{1/2} = R_{CH_3F}/R_{(C_2H_4F_2+C_2H_3F)}{}^{1/2}[\text{ket}]$$

yield

$$k_2/k_4^{1/2} = 2.9 \times 10^3 e^{-4600/RT} \text{ mole}^{-1/2} \text{ cc}^{1/2} \text{ sec}^{-1/2}$$

and

$$k_3/k_5^{1/2} = 1.9 \times 10^3 e^{-6700/RT} \text{ mole}^{-1/2} \text{ cc}^{1/2} \text{ sec}^{-1/2}$$

Limits of error on the activation energies are 0.5 kcal mole^{-1} for reaction 2 and 0.2 kcal mole^{-1} for reaction 3. The latter result fits the general picture for these abstractions,[3,4] but E_2 appears to be exceptionally low. However, we have also obtained[11] a low activation energy, 4.3 kcal mole^{-1}, for the reaction

$$CH_3 + CHF_2COCHF_2 \longrightarrow CH_4 + CF_2COCHF_2$$

The frequency factor ratios for all of these reactions tend to be low, which would imply[11] that the activation energies should each be raised by about 1 kcal mole^{-1}.

Radical-Radical Interactions. The cross-combination ratio for CH_3 and CH_2F is given by

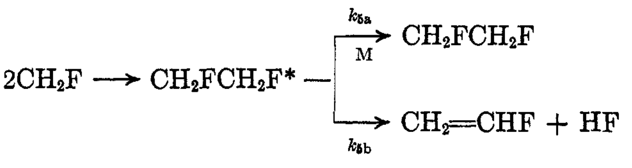
$$k_6/k_4^{1/2}k_5^{1/2} = R_{(C_2H_5F+C_2H_4)}/R_{C_2H_6}^{1/2}R_{(C_2H_4F_2+C_2H_3F)}^{1/2}$$

where

$$CH_3 + CH_2F \longrightarrow C_2H_5F \text{ or } C_2H_4 + HF \qquad (6)$$

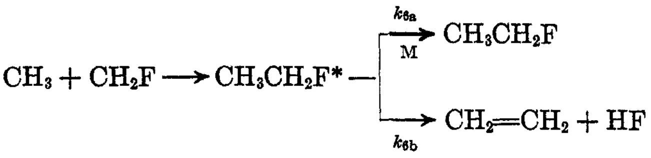
The average value for the ten experiments in Table II, where $C_2H_4F_2$ analyses were obtained, is 2.4. Collision theory predicts a value of 2.3, using collision diameters $\sigma_{CH_3} = 3.5$ A and $\sigma_{CH_2F} = 4.0$ A and assuming that the reactions have identical activation energies and steric factors, usually taken to be zero and unity, respectively.

The elimination of HF can occur from the vibrationally excited fluoroethanes originally produced by radical combination in reaction sequences 5 and 6.



$$2CH_2F \longrightarrow CH_2FCH_2F^* - \begin{cases} \xrightarrow[M]{k_{5a}} CH_2FCH_2F \\ \xrightarrow[k_{5b}]{} CH_2{=}CHF + HF \end{cases} \qquad (5)$$

and



$$CH_3 + CH_2F \longrightarrow CH_3CH_2F^* - \begin{cases} \xrightarrow[M]{k_{6a}} CH_3CH_2F \\ \xrightarrow[k_{6b}]{} CH_2{=}CH_2 + HF \end{cases} \qquad (6)$$

where M represents a third body necessary for collisional deactivation processes.

The temperature dependencies for $k_{5a}/k_{5b} = R_{C_2H_4F_2}/R_{C_2H_3F}[M]$, and $k_{6a}/k_{6b} = R_{C_2H_5F}/R_{C_2H_4}[M]$ are given in Figure 2, where [M] is the pressure of the reacting ketone. The data in Figure 2 is taken from the ten experiments in Table II for which complete analyses are given.

The pressure dependencies for the stabilization/elimination ratios at 406°K are given in Figure 3, showing the expected trend with increasing pressure.[3,5]

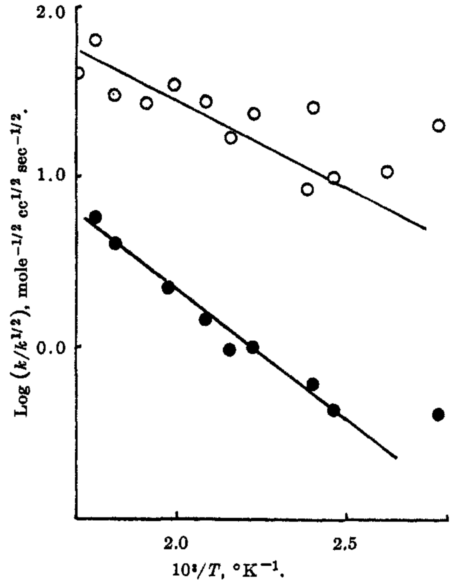


Figure 1. Arrhenius plots for H atom abstraction from CH_2FCOCH_3: ○, log ($k_2/k_4^{1/2}$); ●, log ($k_3/k_5^{1/2}$).

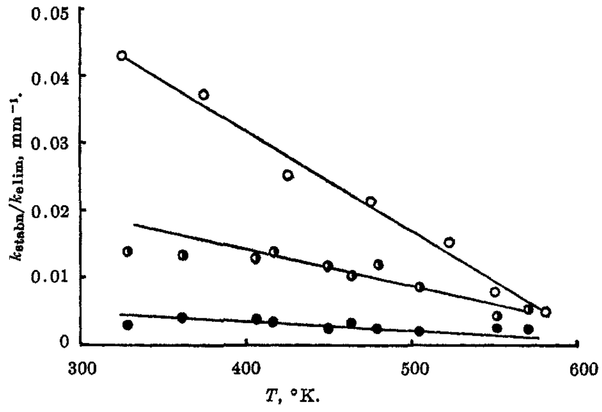


Figure 2. Temperature dependence of $k_{stabilization}/k_{elimination}$: ●, k_{6a}/k_{6b}; ◐, k_{5a}/k_{5b}; ○, k_{5a}/k_{5b}, $(CH_2F)_2CO$ photolysis.[3]

(The points in Figure 2 at 406°K correspond arbitrarily to the high-pressure points, >50 mm, in Figure 3, as the slopes of the lines are not constant.) In Figure 4 the ratio $R_{C_2H_5F}/R_{C_2H_4}$ is shown as a function of the pressure of an added gas (perfluorocyclohexane and perfluorohexane) at constant ketone pressure (4 cm) at 382°K.

Discussion

The rate of HF elimination from a vibrationally excited fluoroethane molecule will depend upon (a) the vibrational energy content of the "hot" molecule, (b) the F atom content and distribution in the molecule,

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[11] J. T. Bryant and G. O. Pritchard, to be published.

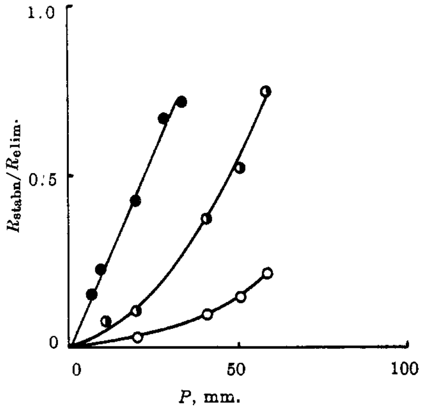

Figure 3. Pressure dependence of the stabilization/elimination rate ratios for $C_2H_5F^*$ and $C_2H_4F_2^*$. P represents the initial pressure (mm) of ketone: ○, $R_{C_2H_5F}/R_{C_2H_4}$ (405°K); ◑, $R_{C_2H_4F_2}/R_{C_2H_3F}$ (405°K); ●, $R_{C_2H_4F_2}/R_{C_2H_3F}$ (475°K), $(CH_2F)_2CO$ photolysis.[3]

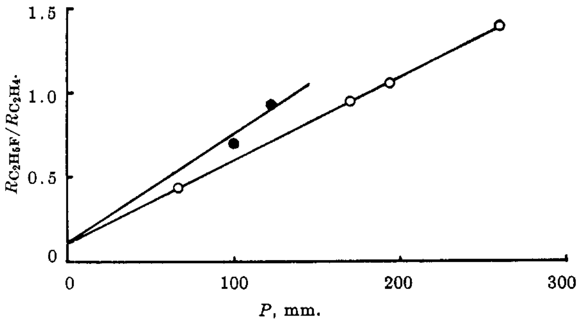

Figure 4. Pressure dependence of $R_{C_2H_5F}/R_{C_2H_4}$ in the presence of an added gas. P represents the pressure (mm) added to 40 mm of CH_2FCOCH_3 at 382°K: ○, $c\text{-}C_6F_{12}$; ●, $n\text{-}C_6F_{14}$.

and (c) the nature of the environment with respect to collisional quenching.

(a) The initial vibrational energy content of the "hot" molecule is primarily a function of the strength of the C–C bond which is formed on radical combination and the temperature of the system. Based on a number of factors, including the uncertainty in $D(CF_3–CF_3)$ and the weakening of the C–C bond in ethane with increasing chlorination, we have suggested[10] that fluorination may tend to weaken C–C bonds, so that, with increasing fluorination, the energy content of the "hot" fluoroethane, formed by radical combination, will be lowered, tending to a reduced rate of HF elimination. Alternatively, other investigations would suggest that fluorination of ethane increases the C–C bond strength,[12] leading to an enhancement in the rate of HF elimination. The vibrational heat capacity of the molecule will also rise with increasing F atom content.

(b) Assuming equal C–C bond energies in the "hot" molecules $C_2H_5F^*$, $C_2H_4F_2^*$, $C_2H_3F_3^*$, and $C_2H_2F_4^*$, BH[2] estimated relative rates of HF elimination to stabilization from these molecules at 298°K of approximately 400:50:7:1 based on the increasing number of effective oscillators with increasing F atom content of the molecules. This approach gives the best description of the experimental results and there is no doubt that the number of effective oscillators in the "hot" molecule is the predominant factor in determining its fate. However, it should be remembered that the activation energy for HF elimination probably decreases with increasing fluorination, so that the decrease in HF elimination will not be so marked as would be expected. Maccoll[13] has tabulated the activation energies for the unimolecular dehydrohalogenations in the pyrolyses of the haloethanes C_2H_5Cl, $C_2H_4Cl_2$, and $C_2H_3Cl_3$, and C_2H_5Br and $C_2H_4Br_2$; there is a distinct decrease in activation energy with increasing halogenation. Further, the elimination from $CH_2FCH_2F^*$ will not necessarily be identical with that for $CH_3CHF_2^*$, as α halogenation tends to promote the rate of dehydrohalogenation relative to β halogenation.[13] We are currently investigating[11] these effects through the interactions of the radical pairs $CH_3 + CHF_2$ and $CH_2F + CHF_2$.

(c) For a given temperature and a given collision frequency the deactivation rate of a particular "hot" molecule will also be a function of the nature of the deactivating species in the system. For example, Giles and Whittle[5] in their investigation of the hot molecule $CH_3CF_3^*$ find values of $R_{CH_3CF_3}/R_{CH_2=CF_2}$ varying by a factor of 20 at 150° by changing the nature and the pressure of the quenching molecules present in the system.

Treatment of the Data. Based on the treatment of BH[2] for $CH_2FCH_2F^*$ produced in $(CH_2F)_2CO$ photolysis,[3] we may make a kinetic analysis of the present data on $C_2H_5F^*$ and $C_2H_4F_2^*$ in terms of the RRK theory of unimolecular reactions[2] and relate the rate constant k_{5b} (or k_{6b}) to the internal energy content, E, of the molecule. That is

$$k_{5b} \text{ (or } k_{6b}) = A(1 - E^*/E)^{n-1} \qquad (7)$$

where E^* represents the critical energy necessary for decomposition, n is the number of effective oscillators, and A is the frequency factor for the unimolecular

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(12) Although estimates of $D(CF_3–CF_3)$ vary from 65 to 95 kcal $mole^{-1}$ (E. Tschuikow-Roux, *J. Phys. Chem.*, **69**, 1075 (1965)), most recent evidence (E. Tschuikow-Roux, *J. Chem. Phys.*, **43**, 2251 (1965), and H. O. Pritchard, private communication) favors the extreme upper value. W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3450 (1962), calculate $D(CF_3–CH_3)$ as 88 kcal $mole^{-1}$.

(13) A. Maccoll, *Advan. Phys. Org. Chem.*, **3**, 91 (1965).

elimination. Following BH[2] we assume that deactivation occurs on a single collision and the rate of collisional deactivation can be written as

$$k_{5a} \text{ (or } k_{6a}) = QZ \qquad (8)$$

where Z is the number of collisions per second per millimeter and Q represents the probability of complete deactivation on collision. From a cascade (see later) point of view $1/Q$ represents the average number of collisions required for deactivation below the threshold energy for elimination. From eq 7 and 8 we have

$$\frac{k_{5a}}{k_{5b}} = \frac{1}{P}\frac{R_{C_2H_4F_2}}{R_{C_2H_5F}} = \frac{QZ_{5a}}{A_{5b}}\left[\frac{E}{E - E^*}\right]^{n-1} \qquad (9)$$

where P is the third-body pressure in millimeters. A similar equation represents k_{6a}/k_{6b}. The temperature dependence of the ratio k_{5a}/k_{5b} is assumed[2] to be due to the temperature dependence of E and the temperature dependencies of the collision terms QZ are neglected.[14]

$E(T)$ for $C_2H_4F_2^*$ has been estimated by BH[2] and the function for $C_2H_5F^*$ may be estimated in a similar manner and is given in Table IV, where ΔC_v^{vib} is defined as the difference in vibrational specific heat of the two radicals and the hot molecule and

$$E = E_0 + \Delta C_v^{\text{vib}}(T - 298)$$

where E_0 is the energy change on combination, taken to be 85.4 kcal mole^{-1}.

The experimental data and some representative theoretical curves computed from eq 9 are given as a function of temperature in Figures 5 and 6 for k_{5a}/k_{5b} and Figures 7 and 8 for k_{6a}/k_{6b}. The curve fitting was performed by choosing a suitable value for log (QZ/A), which shifts the curve vertically. The choice of values of n and E^* to obtain a fit is somewhat arbitrary.[2] The curves have been fitted to the experimental data in Figures 5 and 7 in the temperature range 400–500°K as we consider that the analysis for the products in question, particularly C_2H_5F, is the most accurate in this range (see Table II). An exact fit is not, in any case, to be expected, owing to the neglect of the influence of temperature on n, Q, and Z. Except for the experiments at the lowest and highest temperatures, where the C_2H_5F yields were low, the correlation in Figure 7

Table IV: Internal Energy of $CH_3CH_2F^*$

T, °K	Thermal energy,[a] $\Delta C_v^{\text{vib}}(T - 298)$, kcal mole^{-1}	E, kcal mole^{-1}
298	0	85.4
329	0.5	85.9
362	1.1	86.5
406	2.1	87.5
417	2.3	87.7
450	3.1	88.5
464	3.5	88.9
480	4.0	89.4
505	4.7	90.1
552	6.3	91.7
570	7.0	92.4

[a] The change in the internal energy with temperature was calculated from $\Delta C_v^{\text{vib}}(T - 298) = 3R(T - 298) + [C_{v,CH_3}^{\text{vib}}(T) + C_{v,CFH_2}^{\text{vib}}(T)]T - [C_{v,CH_3}^{\text{vib}}(298) + C_{v,CFH_2}^{\text{vib}}(298)]298$. Vibrational contributions to the heat capacities of CH_3 and CFH_2 were estimated from the heat capacities of CH_4 and CFH_3, respectively.

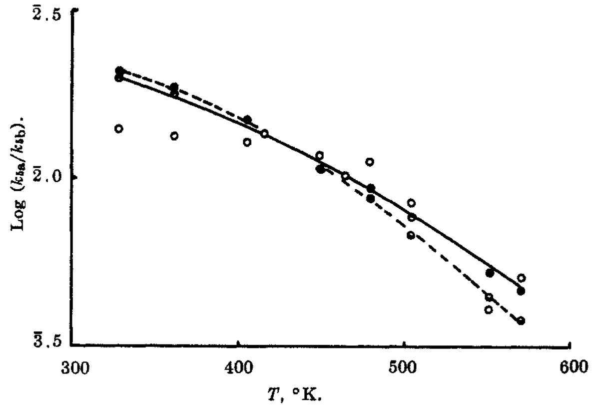

Figure 5. Comparison of the theoretical and observed temperature dependence of k_{5a}/k_{5b} for n = 11: ○, experimental points; ◓, E^* = 59 kcal mole^{-1}, log $(QZ/A) = -6.75$; ◒, E^* = 62 kcal mole^{-1}, log $(QZ/A) = -7.24$.

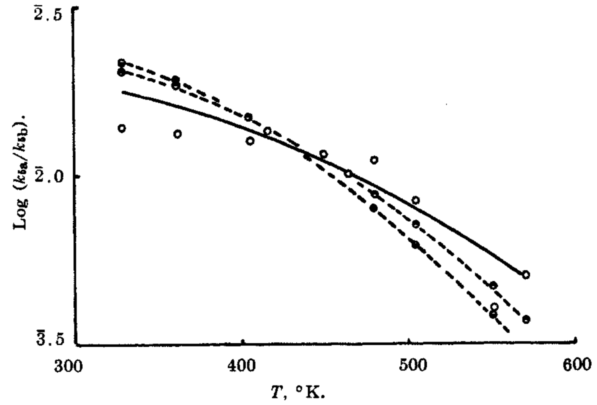

Figure 6. Comparison of the theoretical and observed temperature dependence of k_{5a}/k_{5b} for n = 12: ○, experimental points (solid line); ◓, E^* = 59 kcal mole^{-1}, log (QZ/A) = -7.24; ◒, E^* = 62 kcal mole^{-1}, log $(QZ/A) = -7.77$.

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[14] These are expected[2] to be much smaller than $E(T)$ and are also compensatory, as values of Q decrease with increasing temperature; see J. R. Dacey, R. F. Mann, and G. O. Pritchard, *Can. J. Chem.*, **43**, 3215 (1965), and D. H. Shaw and H. O. Pritchard, *J. Phys. Chem.*, **70**, 1230 (1966).

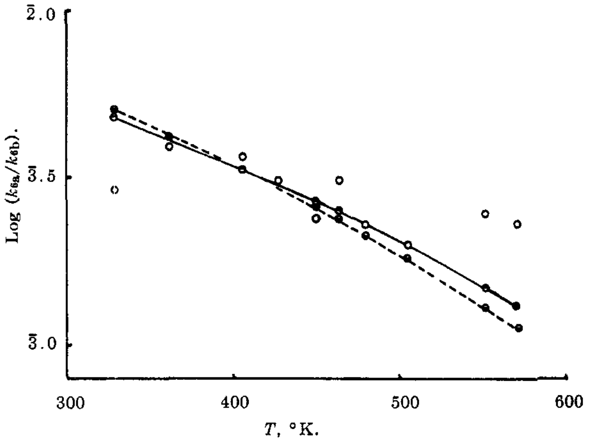

Figure 7. Comparison of the theoretical and observed temperature dependence of k_{6a}/k_{6b} for $n = 10$: ○, experimental points; ◓, $E^* = 59$ kcal mole^{-1}, log $(QZ/A) = -6.86$; ◒, $E^* = 62$ kcal mole^{-1}, log $(QZ/A) = -7.29$.

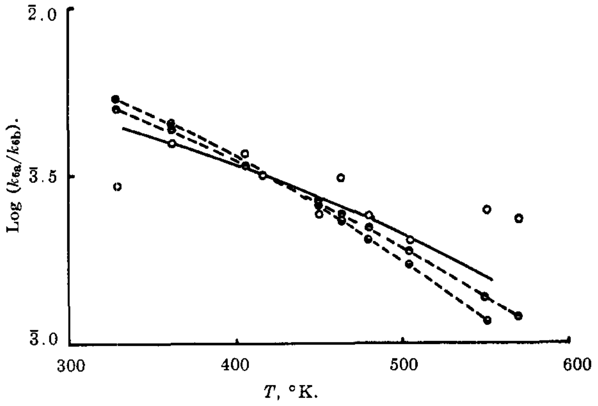

Figure 8. Comparison of the theoretical and observed temperature dependence of k_{6a}/k_{6b} for $n = 11$: ○, experimental points (solid line); ◓, $E^* = 59$ kcal mole^{-1}, log $(QZ/A) = -7.34$; ◒, $E^* = 62$ kcal mole^{-1}, log $(QZ/A) = -7.83$.

for $C_2H_5F^*$ with values of $n = 10$ and $E^* = 59$ kcal mole^{-1} appears to be satisfactory. We have tended to ignore the two low-temperature points in Figure 5. Flatter curves may be obtained by lowering E^* for a particular n or lowering n for a particular E^*, but in view of the expected values of these parameters[2] for $C_2H_4F_2^*$ we have adopted $n = 11$ and $E^* = 59$ kcal mole^{-1}.

Assuming collision diameters of 5.0 A for the two fluoroethanes and a collision diameter of 5.5 A for monofluoroacetone, the collisions frequencies are $Z_{5a} = 10^{7.07}$ and $Z_{6a} = 10^{7.11}$ mm^{-1} sec^{-1} at 298°K. Taking[2,13] $A_{5b} = A_{6b} = 10^{13.5}$ sec^{-1}, we may calculate values of Q from Figures 5, 6, 7, and 8. These are given in Table V. The values of Q obtained with $n = 11$ and $E^* = 59$ kcal mole^{-1} for k_{5a}/k_{5b} and with $n = 10$ and $E^* = 59$ kcal mole^{-1} for k_{6a}/k_{6b} are 0.47 and 0.34, respectively.

Table V: Variation of Q with Different Choices of n and E^*

	E^*, kcal mole^{-1}	n		n^a	
		11	12	11	12
k_{5a}/k_{5b}	59	0.47	0.15	1.3	0.41
	62	0.15	0.046	0.43	0.13
		n			
		10	11		
k_{6a}/k_{6b}	59	0.34	0.11		
	62	0.14	0.036		

[a] Data of BH[2] with $(CH_2F)_2CO$ as the quenching molecule.

The "hot" fluoroethane molecules formed in these systems must lose about 25 kcal mole^{-1} of excess vibrational energy by collision, before they fall below the threshold for HF elimination. Rabinovitch and his co-workers[15] have made extensive studies of the quenching of "chemically activated" species, finding that on the average the amount of vibrational energy transferred on collision may vary between 2 and >15 kcal mole^{-1}, depending mainly on the complexity of the quenching molecules. From the variation in the values of Q given in Table V, no exact assessment of the magnitude of the vibrational energy transferred on collision in these systems can be made. The uncertaintity in the Q values is evidenced by the physically meaningless value of 1.3 given for $C_2F_4H_2^*$, for $n = 11$, and $E^* = 59$ kcal mole^{-1} in the $(CH_2F)_2CO$ system.[2] However, these values of the parameters do not represent the best fit for the "hot" molecule; BH[2] suggest $n = 12$ and $E^* = 62$ kcal mole^{-1}, with a value of $Q = 0.13$, as a good representation of the system. Taken in conjunction with the present data on $C_2H_4F_2^*$, it would seem that values of n between 11 and 12 and E^* between 59 and 62 kcal mole^{-1} give an adequate description of the "hot" molecule, formed by CH_2F recombination. Once n and E^* are chosen, identical values of Q are not to be expected for the two systems, owing to the differing deactivation efficiencies of the two molecules $(CH_2F)_2CO$ and CH_2FCOCH_3.

From the slopes and the intercepts in Figure 4 it is possible to show that (see eq 11, given later) the perfluorocyclohexanes are two to three times more efficient deactivators than the ketone, indicating that $Q < 0.5$ for the ketones; BH[2] recommend a value of 0.1–0.2, which seems to be justifiable.

In Figure 2 it is seen that the rate of HF elimination from $C_2H_5F^*$ exceeds that from $C_2H_4F_2^*$ in accord with the increase in effective oscillators in the latter

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(15) See F. Fletcher, B. Rabionvitch, K. Watkins, and D. Locker, *J. Phys. Chem.*, **70**, 2823 (1966), for a recent summary.

molecule. At 298°K the experimental value of $(k_{6a}/k_{6b})/(k_{5a}/k_{5b})$ is about 0.25 in Figure 2. Using the values that we have recommended we see that

$$\frac{(k_{6a}/k_{6b})_{\ 298°\text{K}}}{(k_{5a}/k_{5b})_{\ 298°\text{K}}} = \frac{10^{-6.86}\left(\dfrac{85.4}{85.4 - 59}\right)^{9}}{10^{-6.75}\left(\dfrac{85.4}{85.4 - 59}\right)^{10}} = 0.24$$

In their analysis BH[2] suggest a value of 0.14 for this ratio. The agreement is satisfactory, as it should be noted that provided values of QZ/A and E^* are reasonable and not markedly different, such ratios are dependent mainly on the choice of the change in n, Δn, when a C–H oscillator is replaced by a more effective (lower frequency) C–F oscillator. Ratios of about 0.2 are readily computed assuming Δn = 1–1.5 for the replacement of an H atom by an F atom in the "hot" molecule.

The two sets of data in Figure 2 on $C_2H_4F_2{}^*$ are best interpreted by assuming that $(CH_2F)_2CO$ is a more efficient energy acceptor than is CH_2FCOCH_3, so that stabilization is relatively more favored with the heavier ketone. In Table V, for a particular choice of n and E^*, it is seen that $Q_{(CH_2F)_2CO}$ exceeds $Q_{CH_2FCOCH_3}$ by a factor of about 3.[16] As Q decreases and the energy content of the molecules increases, with increasing temperature, this difference becomes less important at higher temperatures, as the rate of deactivation below the threshold energy for HF elimination becomes slower; eventually a stage may be reached in either system where most of the "hot" molecules have time to eliminate HF from some level on the vibrational cascade. At extremely high temperatures this is seen to be the case. For example, although very little HF elimination occurs from $C_2H_2F_4{}^*$[17] and $C_2HF_5{}^*$ at normal temperatures,[4] primarily owing to the increase in the effective oscillators in these molecules,[2] at 1200–1600°K Tschuikow-Roux[18] finds $R_{C_2HF_5}/R_{C_2F_4} < 0.02$ for $C_2HF_5{}^*$.

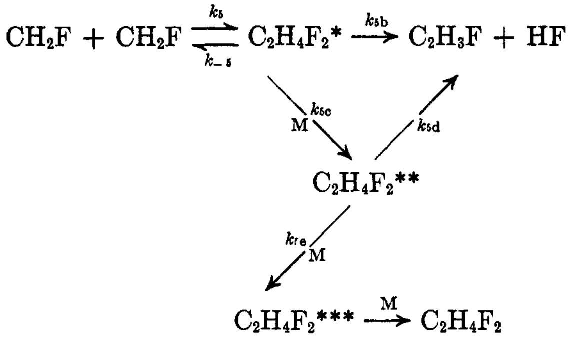
Pressure Effects. In the presence of an added third body, M, we have eq 10 and 11 for the two stabilization/elimination ratios, as the deactivating efficiency

$$R_{C_2H_4F_2}/R_{C_2H_3F} = (k_{5a}[CH_2FCOCH_3] + k_{5a}'[M])/k_{5b} \quad (10)$$

$$R_{C_2H_5F}/R_{C_2H_4} = (k_{6a}[CH_2FCOCH_3] + k_{6a}'[M])/k_{6b} \quad (11)$$

of M is not necessarily the same as for the ketone.[5] The linearity predicted by eq 11 for constant ketone concentration and varying [M] is shown in Figure 4 and the intercepts are in agreement with the expected value of $R_{C_2H_5F}/R_{C_2H_4}$ at [M] = 0 and 4-cm pressure of ketone at 382°K.

When ketone only is present, *i.e.*, [M] = 0, eq 10 and 11 predict that the stabilization/elimination ratios are linear functions of the ketone concentration passing through the origin. In Figure 3 it is seen that the data on $C_2H_4F_2{}^*$ in the difluoroacetone system[3] at 478°K are in accord with this simple mechanism,[2] *i.e.*, reaction 5 where M is $(CH_2F)_2CO$. However, in the same figure, it is seen that the data on $C_2H_4F_2{}^*$ and $C_2H_5F^*$, obtained in the present work, tend to show curvature, which is not completely in accord with the simple mechanism as depicted by reactions 5 and 6. Adopting a cascade mechanism for deactivation, we may consider the simplest case of a two-step deactivation process to a molecule $C_2H_4F_2{}^{***}$ which has insufficient energy to eliminate HF



Now $R_{C_2H_4F_2} = k_{5e}[M][C_2H_4F_2{}^{**}]$ and $R_{C_2H_3F} = k_{5b}[C_2H_4F_2{}^*] + k_{5d}[C_2H_4F_2{}^{**}]$. Assuming a steady state for $C_2H_4F_2{}^{**}$, we have

$$d[C_2H_4F_2{}^{**}]/dt = 0 = k_{5c}[M][C_2H_4F_2{}^*] - k_{5d}[C_2H_4F_2{}^{**}] - k_{5e}[M][C_2H_4F_2{}^{**}]$$

and

$$\frac{R_{C_2H_4F_2}}{R_{C_2H_3F}} = \frac{k_{5c}k_{5e}[M]^2}{k_{5b}k_{5d} + [M](k_{5b}k_{5e} + k_{5c}k_{5d})} \quad (12)$$

The term in $[M]^2$ would cause upward curvature, as seen in Figure 3, and when [M] = 0, the ratio $R_{C_2H_4F_2}/R_{C_2H_3F} = 0$. In the region of high pressure the term $k_{5b}k_{5d}$ becomes less important with respect to $[M]\cdot(k_{5b}k_{5e} + k_{5c}k_{5d})$, leading to a linear relationship between $R_{C_2H_4F_2}/R_{C_2H_3F}$ and [M], which our results tend to do.

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[16] This factor appears to be too large; Giles and Whittle[5] find a factor of 2 in the deactivating efficiencies of $(CF_3)_2CO$ and $(CH_3)_2CO$ for the "hot" molecule $CH_3CF_3{}^*$. However, our discussion is presumably qualitatively correct.

[17] At 464°K, $R_{C_2H_2F_4}/R_{C_2HF_3} = 38$ at 0.72 cm pressure of $(CHF_2)_2CO$.[11]

[18] E. Tschuikow-Roux, *J. Chem. Phys.*, **42**, 3639 (1965).

The extent of the curvature is dependent upon the magnitude of the first term in the denominator in eq 12. At 405°K, we may take $k_{5c} = k_{5e} = 10^{7.14}$ mm^{-1} sec^{-1} and $k_{5b} = 10^{13.5}\left(\frac{87.4 - 59}{87.4}\right)^{10} = 4.15 \times 10^{8}$ sec^{-1} and express [M] in millimeters. Assuming $k_{5d} = k_{5b}$, the ratio in eq 12 reduces to $[\mathrm{M}]^2/(980 + 60[\mathrm{M}])$, which almost exactly represents the experimental curve for $C_2H_4F_2{}^*$ for the present system in Figure 3. As the internal energy of $C_2H_4F_2{}^{**}$ is reduced below that of $C_2H_4F_2{}^*$, we should take a value of $k_{5d} < k_{5b}$. Assuming $k_{5d} = 0.1k_{5b}$, the ratio in eq 12 leads to a line of lesser curvature and to values of $R_{C_2H_4F_2}/R_{C_2H_5F}$ that are too big, *e.g.*, 0.23 at 10 mm and 1.4 at 50 mm, both at 405°K. Taking $k_{5d} = 0.1k_{5b}$ leads to an internal energy for $C_2H_4F_2{}^{**}$ of 79.5 kcal mole^{-1} at 405°K, based on $E^* = 59$ kcal mole^{-1} and $n = 11$, for the hot molecule. This is a decrease of 8 kcal mole^{-1} below the internal energy for $C_2H_4F_2{}^*$ at 405°K. A better correlation is obtained by assuming a "weaker" deactivating collision, *e.g.*, $k_{5d} = 0.5k_{5b}$, which corresponds to a drop of about 3 kcal mole^{-1} in the internal energy. ($R_{C_2H_4F_2}/R_{C_2H_5F}$ is 0.11 at 10 mm and 0.93 at 50 mm.) If this amount of energy is transferred per collision by a "hot" molecule while it is on the vibrational cascade, it would take about eight collisions before it falls below the limit for HF elimination, which we may equate with a value of $Q = 0.13$.

Several other more complicated cascade schemes were tried,[19] in particular for cases where there were more than two levels on the cascade from which elimination could occur and where there was competition between a one-step and a two-step deactivation process below the threshold from a particular level on the cascade. Application of the steady-state treatment leads to more involved expressions than eq 12, which predict upward curvature for $R_{C_2H_4F_2}/R_{C_2H_5F}$ with increasing [M] and reduce to zero at $[\mathrm{M}] = 0$.

In the case where M is a very efficient quenching molecule, $C_2H_4F_2{}^{**}$ may be close to or below the threshold for elimination so that $k_{5d} \simeq 0$ and we revert to the simple mechanism, reaction 5, where $k_{5c} = k_{5a}$. From Figure 3, it would therefore appear that $(CH_2F)_2CO$ is an efficient deactivator of $C_2H_4F_2{}^*$. The efficiency of the perfluorohexanes as deactivators for $C_2H_5F^*$ is exemplified in Figure 4. It should be pointed out that this linearity does not mean complete deactivation below the threshold energy on the first collision, *i.e.*, $Q = 1$. However, if a "hot" molecule is sufficiently deactivated by the first collision, its energy level may be such that rate of HF elimination is not significant when compared to the rate from the "hot" molecule before collision; note above that $k_{5d} = 0.1k_{5b}$ corresponds to a decrease of 8 kcal mole^{-1} in internal energy. Our result that $Q_{(CH_2F)_2CO} = 3Q_{CH_2FCOCH_3}$ for $C_2H_4F_2{}^*$ (Figure 2 and Table V) would also seem to be justified (Figure 3).

Summary

It should be noted that our description and that of BH[2] are in good accord. From the known experimental and calculated activation energies for dehydrohalogenation of haloethanes,[2,13] it seems that values for $C_2H_4F_2$ and C_2H_5F are in the range 59–62 kcal mole^{-1}. Once E^* is chosen, it is seen that the value of Q obtained is very sensitive to the value of n. Within the allowable margin of variation for these parameters, there is reasonable agreement between the theoretical model and the experimental systems. In the systems discussed here, $C_2H_5F^*$ and $C_2H_4F_2{}^*$ with the ketones as quenching molecules, we may estimate that somewhere between 3 and 8 kcal mole^{-1} of excess vibrational energy is transferred on collision.

Acknowledgment. G. O. P. wishes to thank Professor J. R. Dacey for his generous hospitality and several helpful discussions during the completion of the manuscript for this article.

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[19] R. L. Thommarson, Ph.D. Thesis, University of California, Santa Barbara, Calif., 1966.