Unimolecular Reaction and Collisional Deactivation of Chemically Activated 1,2-Difluoroethane Produced by Mercury Photosensitization of Chlorofluoromethane at 300 and 475°K[1]

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Abstract: The mercury photosensitization of CH_2ClF mixed with 10% propene was used as a source of CH_2F radicals for the generation of chemically activated 1,2-$C_2H_4F_2$*. The pressure required for stabilization of one-half of the excited molecules was 2.0 ± 0.1 and 4.6 ± 0.2 cm at 300 and 475°K, respectively. The results from low-pressure experiments were used to deduce the collisional deactivation efficiency of CH_2ClF for 1,2-$C_2H_4F_2$*. The experimental data were interpreted using a four-centered HF elimination activated complex model with specific rate constants calculated according to the RRKM formulation of unimolecular reactions with full provision for the thermal distribution function of the chemically activated molecules. Comparison of calculated and experimental results indicates that the critical energy for HF elimination is 62 kcal mol^{-1} and that on the average 11 ± 3 kcal mol^{-1} of energy is removed from $C_2H_4F_2$* per collision with CH_2ClF. Nonequilibrium chemical activation rate constants also were calculated for 1,1-$C_2H_4F_2$ and n-C_3H_7F, and comparison was made with the published experimental data. The temperature dependence of the chemical activation rate constants was of special interest and the question of the temperature dependence of the collisional deactivation cross section was considered. Criticism of earlier classical Kassel treatments of the chemical activation data of these fluoroalkane systems is presented.

The elimination of hydrogen fluoride from chemically activated 1,2-difluoroethane formed by radical association was the first[3] example of a now well-documented class of nonequilibrium unimolecular reactions for fluoroethanes[4–7] and fluoroalkanes.[5,8] There are three published sets of data describing the unimolecular reaction of chemically activated 1,2-$C_2H_4F_2$ formed by photolysis of fluoroacetone[4] and photolysis of 1,3-difluoroacetone.[3,5] However, conflicts between the different sets prevent a clear-cut choice for the temperature dependence and for the values of the chemical activation rate constants. One objective of the present work was to carefully measure the nonequilibrium unimolecular rate constants for 1,2-$C_2H_4F_2$ in a system that did not involve ketone photolysis. The mercury-photosensitized reaction of CH_2FCl with 10% propene was chosen because previous work[9] from our laboratory showed that mercury photosensitization of CH_2Cl_2 with added propene provided an adequate means for studying chemically activated 1,2-$C_2H_4Cl_2$.

A second objective was to measure the stabilization to decomposition product ratio at low pressures ($S/D \leq 0.2$) in order to determine approximate limits for the collisional deactivation model. This was important for comparison of various data in the literature which have been obtained using a variety of bath gases at different temperatures. Data are presented with CH_2ClF as the bath gas which show that essentially unit deactivation rate constants are obtained as long as the measurements are made at pressures sufficiently high so that $S/D \geq 0.5$. This also should be true for bath gases of similar or greater molecular complexity.

The third objective was to apply the four-centered model for H–X elimination developed from chemical and thermal activation kinetic data of chloro-[10] and bromoethanes[11] to the 1,2-difluoroethane reaction. The thermochemistry which includes the critical energy, ϵ_0, and the minimum energy of the formed molecules, $E_{\min} = D_0°(CH_2F{-}CH_2F) + E_{act}(CH_2F + CH_2F)$, is not well known for 1,2-$C_2H_4F_2$, so the magnitudes of the chemical activation rate constants cannot be used for relevant testing of unimolecular reaction rate theory. Instead we have compared the experimental results to calculations using the RRKM[12] formulation of unimolecular reactions with reliable models for the molecule and the activated complex in order to deduce various thermochemical and kinetic items of interest.[13] In particular, by estimating the minimum energy of chemically activated $C_2H_4F_2$ from the heats of formation of CH_2F and $C_2H_4F_2$, it was possible to use the kinetic data to establish the critical energy, ϵ_0, of the reaction. After finding a value for ϵ_0, the temperature dependence of the nonequilibrium rate constants, calcu-

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[1] Abstracted from the thesis of H. W. Chang which was submitted in partial fulfillment for the requirements of the Master's degree, Kansas State University, 1969.

[2] Alfred P. Sloan Foundation Fellow.

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[12] (a) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, 55, 894 (1951); (b) R. A. Marcus, *J. Chem. Phys.*, 20, 352, 359 (1952); 43, 2658 (1965).

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lated from the appropriate thermal distribution function, was compared to the experimental results. Difluoroethane was chosen for this comparison because data in the literature cover a wide temperature range and because RRK calculations[4,5,14] have been used to analyze the data. Some of the conclusions derived from the RRK treatment need to be compared to the more rigorous RRKM interpretations, and we have examined the data for 1,1-$C_2H_4F_2$ and *n*-C_3H_7F as well as 1,2-$C_2H_4F_2$ for this purpose. Evaluation of the chemical activation data on fluoroethane using the RRKM theory has recently been done.[15] However, those calculations differ in several respects from the ones presented here.

Experimental Section

The samples were sensitized in quartz vessels using a General Electric germicidal lamp (G-15T8). Desired pressures were obtained by placing measured quantities of reactants, nearly always 2.0 cc of gas, into various vessels of known volumes. The room-temperature experiments were done with samples saturated with mercury; irradiations were for 20–40 min which normally corresponded to about 2% reaction of starting material. For the 475 ± 10°K experiments, the sealed quartz vessels were placed in a furnace which had a narrow slit along one side. This furnace was placed directly above the photolysis lamp, and the 2537-Å light reached the reaction vessel through the slit. The mercury vapor pressure was maintained approximately at its equilibrium room-temperature value by putting the mercury droplet into a narrow side arm attached to the vessel which extended outside the furnace and was shielded from the lamp.

Gas chromatographic analyses were done by injecting the entire sample onto a 16-ft Porapak-S column; the chromatograph had a thermal conductivity detector. With appropriate temperature programming, the relevant products could be separated in a single pass. The eluted peaks were identified from retention times of authentic samples and also from their mass spectral cracking patterns. Quantitative measurements of product yields were made by comparison with empirical calibrations. These calibration samples were prepared replicas of sensitized samples, and the calibrations were frequently checked. The data shown in this paper were collected over a 6-month period with frequent cross checking of calibration and data points.

Experimental and Calculated Results

Reaction Mechanisms. Mercury photosensitization of CH_2ClF without added propene at pressures above 20 cm gave 1,2-difluoroethane, 1-chloro-1,2-difluoroethane, 1,2-dichloro-1,2-difluoroethane, and fluoromethane as major products. These products are consistent with the series of reactions below.

$$Hg(^1S_0) + h\nu\ (2537\ \text{Å}) \longrightarrow Hg(^3P_1) \tag{1}$$

$$Hg(^3P_1) + CH_2ClF \longrightarrow CH_2F + Hg + Cl \tag{2a}$$

$$\longrightarrow CH_2F + HgCl \tag{2b}$$

$$Cl + CH_2ClF \longrightarrow CHClF + HCl \tag{3}$$

$$CH_2F + CH_2FCl \longrightarrow CH_3F + CHFCl \tag{4}$$

$$CH_2F + CH_2F \longrightarrow CH_2F\text{–}CH_2F^* \tag{5}$$

$$CH_2F + CHClF \longrightarrow CH_2F\text{–}CHClF^* \tag{6}$$

$$CHClF + CHClF \longrightarrow CHClF\text{–}CHClF^* \tag{7}$$

The above primary reactions of $Hg(^3P_1)$ with CH_2ClF are similar to those found for mercury photosensitization of CH_2Cl_2[9] and CHF_2Cl.[16] For the latter example the quantum yield for generation of CHF_2 was greater than 0.94. In the description to follow it will be shown that the addition of propene removes the chlorine atoms and, hence, prevents the formation of CHClF radicals by reaction 3. If the $Hg(^3P_1)$ directly interacted with CH_2ClF to give CHClF, formation of CH_2F–CHClF in the presence of propene would have been observed. However, this product was not found, and we conclude that reactions 2a and 2b are the only significant primary processes. In contrast to fluoroethane[17a] or fluoromethane,[17b] direct interaction between $Hg(^3P_1)$ and the C–H bond does not seem to take place, or at least not at a rate competitive with reactions 2. No obvious evidence was found to suggest the occurrence of CH_2F or CHFCl disproportionation reactions. Reactions 3 and 4 are hydrogen abstractions with probable activation energies of 2–3 kcal mol^{-1} for Cl[18] and 9–12 kcal mol^{-1} for CH_2F.[19] Reactions 5–7 are combination reactions giving molecules with ~90 kcal mol^{-1} which are collisionally stabilized at high pressures, but at lower pressure they may decompose by HCl and HF elimination.

Our main interest was the rate constant for HX elimination from the chemically activated molecules. These require measurement of the decomposition to stabilization ratio at various pressures. Previous experience[9] has shown that the Cl atoms will remove olefin products from the reaction system, and misleading D/S values will be obtained unless the olefinic decomposition products are protected from attack by Cl atoms.[20] This can be achieved with the addition of propene which reacts rapidly with Cl atoms by reaction 8. Ten per cent propene was sufficient to stop reaction 3, as measured from the disappearance of the CHClF combination products.

$$Cl + CH_3CH{=}CH_2 \longrightarrow CH_3\dot{C}HCH_2Cl \tag{8}$$

With added propene the competition between unimolecular reaction and collisional deactivation of $C_2H_4F_2^*$, reaction 9, can be studied since the decomposition product is not removed from the system. No effort was made to identify all of the expected radical–radical reaction products in the propene + CH_2ClF system. However, a sufficient number were identified to show that CH_2F and $CH_3\dot{C}HCH_2Cl$ were the major radicals in the system. Another radical which enters into the reaction scheme is $\dot{C}H_2CH{=}CH_2$, which is formed by the mercury photosensitization of propene.[21] This radical tends to become more important at lower pressures because the mercury photosensitization of propene involves an excited state[21] which can be collisionally quenched.

$$1,2\text{-}C_2H_4F_2^* \xrightarrow{k_a} HF + C_2H_3F\ (D) \tag{9a}$$

$$\xrightarrow{k_M[M]} 1,2\text{-}C_2H_4F_2\ (S) \tag{9b}$$

Chemical Activation Rate Constants for 1,2-$C_2H_4F_2$. The decomposition to stabilization product ratio was

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

[15] A. W. Kirk, A. F. Trotman-Dickenson, and B. L. Trus, *J. Chem. Soc., A*, 3058 (1968).

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[18] C. Cillien, P. Goldfinger, G. Huybrechts, and G. Martens, *ibid.*, 63, 1631 (1967).

[19] R. D. Giles, L. M. Quick, and E. Whittle, *ibid.*, 63, 662 (1967). The activation energy for H abstraction by CH_2F is probably about the same as for CH_3 or CF_3.

[20] Chlorine atoms react some 200 times faster with olefins (propene) than with CH_2Cl_2. A similar difference in rate between propene and CHClF would be expected.

[21] (a) M. Avrahami and P. Kebarle, *J. Phys. Chem.*, 67, 354 (1963); (b) R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, 37, 543 (1962).

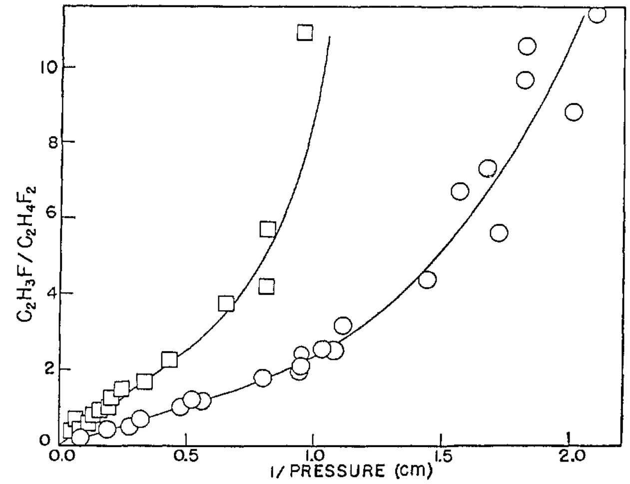

Figure 1. Summary of all data plotted as C_2H_3F/1,2-$C_2H_2F_2$ *vs.* pressure^{-1}. Pressure units are cm; ○, 300°K; □, 475°K.

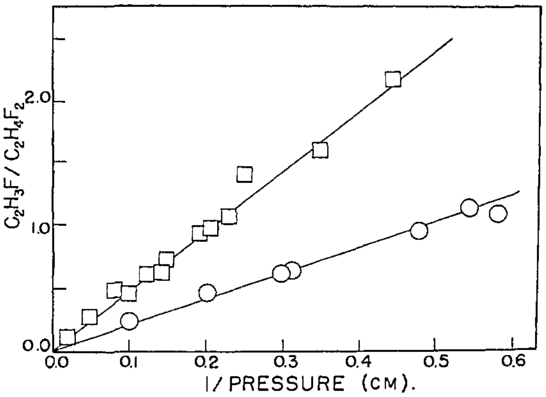

Figure 2. D/S *vs.* pressure^{-1} for the high-pressure data; ○, 300°K; □, 475°K. The slopes give k_a/k_M.

measured over a pressure range sufficiently wide to give S/D values from 10 to 0.1 at 300 and 475°K. The data of Figure 1 show that for D/S < 2.0 a linear relation exists between $1/P$ and D/S; however, at low pressure the data show curvature characteristic of cascade deactivation.[22] Figure 2 is an expansion of the high-pressure data; least-squares analysis gave 2.0 ± 0.1 and 4.6 ± 0.2 cm for the 300 and 475°K values for the slopes, k_a/k_M, of the lines. Two problems, which are discussed below, must be considered before the slopes of these lines can be related to the unit deactivation rate constants.

First, since the data show evidence for cascade deactivation at low pressures, even the high-pressure rate constants are not quite unit deactivation rate constants. Rather they are somewhat larger and are approximately the *sum* of the specific rate constants for the steps of the cascade.[23] Specific rate constants, k_ϵ, are described in the next section, and in a later section they are used to deduce the cascade step size from the low-pressure data. For relatively efficient gases, such as CH_2ClF, the rate constant obtained from the linear part of D/S plot may be multiplied by constant factors, which are obtained from the analysis of the low-pressure data, to obtain the equivalent unit deactivation rate constant. These factors are 0.89 and 0.86 at 300 and 475°, respectively, for a simple stepladder model with an increment of energy transferred per collision, $\langle \Delta E \rangle$, of 11 kcal mol^{-1}.

The second problem is the selection of the collision diameters for the calculation of the collision number, k_M, at the two temperatures in question. Normally temperature-independent diameters (usually the Lennard-Jones σ value) are used. We have made this choice for the lower temperature and used $\sigma_{C_2H_6} = 4.7$, $\sigma_{CH_2ClF} = 4.5$, and $\sigma_{C_2H_4F_2} = 5.0$ Å; the last two were chosen by analogy with CH_2Cl_2 and CH_3COCH_3.[24] These cross sections give a 300°K rate constant, k_a, of 2.0 ± 0.1 × 10^8 sec^{-1}, which is 1.8 ± 0.1 × 10^8 sec^{-1} when converted to a unit deactivation basis. By analogy to transport properties of gases with large ϵ/k values, it seems likely that collision diameters, as well as the cascade mechanism,[22] for vibrational energy transfer may be temperature dependent. One way of allowing for this is to use Ω integrals,[25] which are based upon the temperature dependence of viscosity data. We used the tabulations of ref 24 and estimated that ϵ/k would be 400; actually the ratio $\Omega^{*2,2}(T)/\Omega^{*2,2}(300)$ does not depend strongly upon ϵ/k for large values of ϵ/k and T > 300. The factor relating $\Omega^{*2,2}(300)$ to $\Omega^{*2,2}(475)$ is 0.80. Thus, the experimental rate constant at 475°K is 3.7 ± 0.2 or 3.0 ± 0.2 10^8 sec^{-1} depending upon whether or not allowance is made for the change of the collision diameter with temperature. Converting to unit deactivation gives 3.2 ± 0.2 and 2.6 ± 0.2 × 10^8 sec^{-1}, respectively. We could equally well use $s^2 = \sigma^2\Omega^{*2,2}(T)$ as the cross section at 300°. The only change would be to increase the absolute values[24] of the rate constants at both temperatures. The question of the temperature dependence of these nonequilibrium rate constants is more fully considered in the Discussion section.

RRKM Calculated Rate Constants for 1,2-$C_2H_4F_2$. The specific rate constants are calculated from expression I. In order to calculate k_ϵ one needs to know σ,

$$k_\epsilon = \frac{\sigma P_1^\dagger}{h P_1^*} \sum_{\epsilon_v^\dagger=0}^{\epsilon^\dagger} P(\epsilon_v^\dagger)/N^*(\epsilon) \qquad \text{(I)}$$

the reaction path degeneracy; the model of the activated complex for computation of $P_1^\dagger$ (partition function for over-all rotation) and $\Sigma P(\epsilon_v^\dagger)$ (sum of internal energy eigen states); the moments of inertia and molecular frequencies of the molecule for evaluation of P_1^* (partition function for over-all rotation) and $N^*(\epsilon)$ (density of internal energy eigen states); and the thermochemistry of reactions 5 and 9a. For the haloethanes[10,11] all internal degrees of freedom are active, and the over-all rotations are adiabatic for both the molecule and the complex. Harmonic oscillator sums and densities were used in eq I. The frequencies and moments of inertia for 1,2-$C_2H_4F_2$ are known[26,27] and are summarized in Ta-

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[22] G. H. Kohlmaier and B. S. Rabinovitch, *J. Chem. Phys.*, 38, 1692, 1702 (1963).

[23] D. W. Setser and J. C. Hassler, *J. Phys. Chem.*, 71, 1364 (1967).

[24] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1964, p 1212. Actually collision cross sections, $s^2 = \sigma^2\Omega^{*2,2}(T)$, probably should be used to calculate the collision number at 300°K. However, owing to lack of detailed knowledge for values of σ for CH_2ClF and $C_2H_4F_2$, this point is not worth pursuing.

[25] Y. N. Lin, S. C. Chan, and B. S. Rabinovitch, *J. Phys. Chem.*, 72, 1932 (1968). These authors give a thorough discussion of the possible relations between the Ω integrals and collision cross sections.

[26] P. Klaboe and J. R. Nielsen, *J. Chem. Phys.*, 33, 1764 (1960).

[27] D. C. Smith, R. A. Saunders, J. R Nielsen, and E. E. Ferguson, *ibid.*, 20, 847 (1952).

Table I. Models for 1,2-$C_2H_4F_2$ Molecule and Elimination Complex

Molecule[a]		Complex	
Moments of inertia, amu Å^2	Frequencies,[c] cm^{-1}	Moments of inertia, amu Å^2	Frequencies,[b] cm^{-1}
141	2974 (4)	127	3050 (3)
128.8	1372 (4)	75.2	1337 (3)
18.6	1056 (3)	33.6	1034 (3)
	852 (3)		920 (5)
	542 (2)		604 (1)
	320 (1)		466 (2)
	196 (1)[c]		

[a] The moments of inertia and frequencies[26] are for the *trans* conformation of 1,2-$C_2H_4F_2$; apparently the stability of the *trans* and *gauche* isomers are nearly equal in the gas phase. [b] The three frequencies categories are: ring puckering [450]; in-plane ring [1220, 1130, 960, 600]; and out of ring [3050 (3), 1400 (2), 1000 (2), 920 (2), 905 (2), and 483]. The 483 frequency is the C–C–F bending vibration. [c] The torsional motion was treated as a vibration with frequency of 196 cm^{-1}. The 1,2-$C_2H_4X_2$ molecules usually have high barriers to internal rotation. Apparently the *trans* and *gauche* barrier for 1,2-$C_2H_4F_2$ has not been measured, but by analogy to other fluoroethanes (A. B. Tipton, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **46**, 1606 (1967)) it should be between 3 and 4 kcal mol^{-1}. The barrier for direct conversion from *gauche* to *gauche* is probably much higher (T. E. Piercy, *ibid.*, **43**, 4066 (1965)). Reference 10 contains a discussion of the problem that the torsional motion presents in evaluating $N^*(\epsilon)$ for haloethanes.

ble I. Only α,β elimination[28] occurs from 1,2-substituted fluoroethanes, so a four-centered complex is the proper geometry. The frequencies and moments of inertia for the complex were obtained from the empirical bond-order treatment of the four-centered complex model as described in our earlier work.[10,11] In this calculation we used Johnston's force constant relationships[29] with bond orders of 1.9, 0.9, 0.1, and 0.1 for the C–C, C–F, F–H, and C–H bonds, respectively. The frequencies, which are divided into in-plane-ring, and ring-puckering, and out-of-ring categories, are listed in Table I. The latter were obtained from our previous model for the C_2H_5Cl complex with exchange of three C–H-type vibrations for C–F-type vibrations. The ring-puckering frequency was set 50 cm^{-1} higher than the value used for the four-centered ring containing the chlorine atom.[10b] The models of Table I with a reaction path degeneracy of four gave[30] a preexponential factor, in terms of the partition function ratio, at 800°K of 2.0 × 10^{13} sec^{-1}, which is consistent with previous 1,2-$C_2H_4Cl_2$ and 1,2-$C_2H_4Br_2$ models. Another method for assigning the frequencies to the activated complex for H–X elimination has been proposed.[31] In general it less satisfactorily represents the data for chloroethanes[10b] than does the asymmetric four-centered model developed by our laboratory, although it may be easier to use for describing qualitative features of the reaction.

The critical energy for H–F elimination from 1,2-$C_2H_4F_2$ is not well known; therefore, k_ϵ values were calculated for a range of ϵ_0's, and they are shown in Figure 3. In the 90-kcal mol^{-1} region a change in ϵ_0 by 2 kcal causes a change in k_ϵ by about a factor of 1.9. To

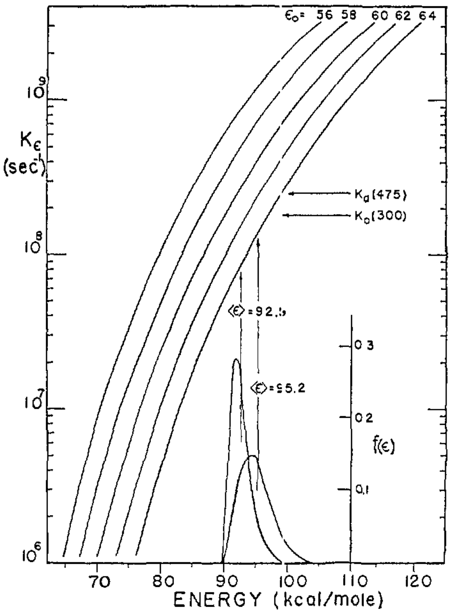

Figure 3. Calculated RRKM rate constants for various values of ϵ_0 and distribution functions at 300 and 475°K for 1,2-$C_2H_4F_2$. The values of the experimental rate constants are indicated by the two arrows.

place the distribution function of formed 1,2-$C_2H_4F_2^*$ molecules on the energy scale, the E_{min} value must be estimated. This requires knowledge of $\Delta H_f{}^\circ{}_0(CH_2F)$ and $\Delta H_f{}^\circ{}_0(C_2H_4F_2)$. The values presented in the Appendix, combined with 1.0 kcal mol^{-1} as the activation energy for reaction 5, gave E_{min} = 89.6 kcal mol^{-1}.

In order to compare calculated and experimental rate constants, the specific rate constants must be averaged over the distribution function of the activated molecules. For unit collisional deactivation the appropriate average is simply

$$k_a = \omega(D/S) = \omega\frac{\int_{E_{min'}}^{\infty}\frac{k_\epsilon}{k_\epsilon + \omega}f(\epsilon)d\epsilon}{\int_{E_{min'}}^{\infty}\frac{\omega}{k_\epsilon + \omega}f(\epsilon)d\epsilon} \tag{II}$$

For simple bimolecular combination reactions the distribution function, f(ε)dε, is defined by eq III[30]

$$f(\epsilon)d\epsilon = \frac{k_\epsilon'K(\epsilon)d\epsilon}{\int_{E_{min}}^{\infty}k_\epsilon'K(\epsilon)d\epsilon} \tag{III}$$

The rate constant, k_ϵ', applies to the dissociation of 1,2-$C_2H_4F_2$ into radicals, *i.e.*, the reverse of the chemical activation formation step, and $K(\epsilon)$ is the Boltzmann distribution. The chemical activation distribution function is shown in Figure 3 at 300 and 475°K. The activated complex model for the dissociation of 1,2-$C_2H_4F_2$ was described by characteristic frequencies of two CH_2F radicals plus four low-bending frequencies (150 (2), 100 (2)) and one internal rotation.[32] This model gave a steric factor for radical combination of ~0.02 when combined with the equilibrium constant for $C_2H_4F_2 \rightleftarrows 2CH_2F$. The shape of the distribution function is not very sensitive to the individual frequencies of the association complex.

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(28) M. J. Perona, J. T. Bryant, and G. O. Pritchard, *J. Am. Chem. Soc.*, 90, 4782 (1968).

(29) H. S. Johnston, "Gas Phase Reaction Rate Theory," The Ronald Press Co., New York, N. Y., 1966.

(30) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, 3, 1 (1964).

(31) H. F. O'Neal and S. W. Benson, *J. Phys. Chem.*, 71, 2903 (1967).

(32) H. W. Chang, Master's Thesis, Kansas State University, 1969.

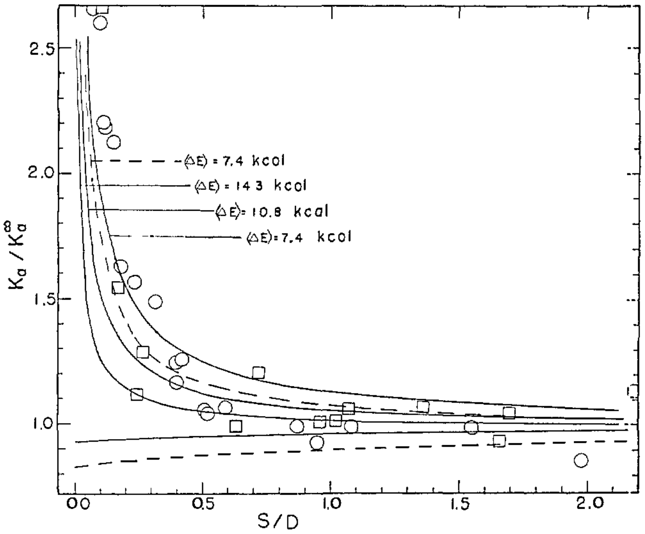

Figure 4. Low-pressure data (○, 300°K; □, 475°K) and calculated curves for simple stepladder cascade deactivation with energy increments of $\langle \Delta E \rangle$ kcal mol^{-1}. The solid and dotted lines are calculated results for 300 and 475°K, respectively. The two bottom curves are the unit deactivation curves. Compared to the unit deactivation value of 1.55×10^8 sec^{-1}, the 300° cascade high-pressure rate constants are k_a^∞ ($\Delta E = 7.4$) = 2.0×10^8, k_a^∞ ($\Delta E = 10.8$) = 1.75×10^8, and k_a^∞ ($\Delta E = 14.3$) = 1.65×10^8 sec^{-1}.

Evaluation of the Critical Energy for 1,2-$C_2H_4F_2$. For low-temperature chemical activation systems with a relatively large difference between E_{min} and ϵ_0, the variation in the unit deactivation k_a between limiting high and low pressures is small; *e.g.*, k_a^∞/k_a^0 is 1.08 at 300° and 1.22 at 475° for $C_2H_4F_2^*$. Thus, the measured high-pressure unit deactivation rate constants can be matched to the k_ϵ that corresponds to the average energy of the 1,2-$C_2H_4F_2^*$ molecules in the manner shown in Figure 3. The best agreement was obtained with the $\epsilon_0 = 62$ kcal mol^{-1} curve. Considering all factors, the reliability of this assignment is probably ± 2 kcal mol^{-1}. The thermal pyrolysis of C_2H_5F recently has been done successfully,[33] and the measured activation energy was 58.2 ($\epsilon_0 = 56.7$) kcal mol^{-1}. A treatment[32] of the chemical activation (CH_3 + CH_2F) kinetic data for $C_2H_5F^*$ in the same way as described here for 1,2-$C_2H_4F_2$ gave virtually perfect ($\epsilon_0 = 57$ kcal mol^{-1}) agreement with the thermally measured value of ϵ_0. This can be taken as further support for our four-centered model for the HX elimination from alkyl halides.

Cascade Deactivation Model. The curvature of the low-pressure data indicates cascade deactivation of 1,2-$C_2H_4F_2^*$. The analysis of the data was done in the same way as previously discussed[23] for 1,2-$C_2H_4Cl_2^*$. The basic procedure is to match the experimental rate constants at low-pressure to the rate constants calculated from a cascade model which has a defined probability of unimolecular reaction and collisional transport for each subregion of the active energy region, *i.e.*, energy above ϵ_0. The comparison of experiment with calculations was done on a plot of k_a/k_a^∞ *vs.* S/D; k_a^∞ is the high-pressure rate constant and k_a is the rate constant corresponding to a particular pressure with an associated value of S/D. The details of the calculations will not be repeated.[23] It is sufficient to note that the active energy region was divided into subregions of 100-cm^{-1} width; a rate constant from Figure 3 ($\epsilon_0 = 62$ kcal mol^{-1}) was associated with each subregion. The collision transition probability model was a simple stepladder cascade through the active energy region in constant increments of variable size, $\langle \Delta E \rangle$ kcal mol^{-1}. The $\langle \Delta E \rangle$ values correspond to the average energy removed from the internal degrees of freedom of $C_2H_4F_2^*$ per collision. The calculated curves and experimental points are shown in Figure 4; each calculated $k_a^\infty\langle \Delta E \rangle$ value is listed in the figure caption. There is an appreciable difference between the calculated curves for the same $\langle \Delta E \rangle$ value at 300 and 475°K as shown by the two 7.4-kcal mol^{-1} curves in Figure 4. In fact the 475° $\langle \Delta E \rangle = 7.4$ curve is approximately equivalent to a $\langle \Delta E \rangle = 9$ kcal mol^{-1} curve at 300°. This difference arises from the greater dispersion in energy of the molecules formed at the higher temperature and is also apparent from the difference in the two unit deactivation curves.

It is clear from Figure 4 that some type of cascade description is appropriate since the experimental k_a values do increase by factors of 2.5 as S/D becomes smaller. Unfortunately the data at the higher temperature are less reliable owing to enhanced side reactions in these radical systems. The second conclusion is that, even for the better data at 300°, no single curve fits the experimental points over the whole S/D range because the experimental k_a/k_a^∞ points obviously rise more abruptly than do the calculated curves. Some adjustment can be made by using a lower experimental value for k_a^∞ which reduces but does not eliminate this trend. The relative change in our experimental k_a^∞ values at the two temperatures is a little less than the calculated result which further suggests that the 300°K experimental k_a^∞ may be a little too high. Nevertheless, form our data a lower limit to the experimental k_a^∞ would be about 1.8 cm. The tendency of the experimental data to cross the calculated curves in the turn-up region of S/D was found in the previous $C_2H_4Cl_2^*$ studies.[23] An exponential model of collision transition probabilities gives an even less desirable fit. These data are not particularly accurate, and it would be premature to judge the stepladder model to be inadequate. The best statement is that the average energy lost per collision of 1,2-$C_2H_4F_2^*$ with CH_2FCl is 11 $\pm$ 3 kcal mole^{-1}. Owing to the experimental error there is no discernible difference between the 300 and 475°K results, although it might have been anticipated, based upon earlier chemical activation results,[22] that the average energy transferred per collision would be smaller at increased temperature.

The average loss per collision[23] of chemically activated $C_2H_4Cl_2$ ($\langle \epsilon \rangle = 88$ kcal mol^{-1}) with CH_3Cl and CH_2Cl_2 was measured as 10–14 kcal mol^{-1} and for cyclopropane[34] ($\langle \epsilon \rangle \cong 100$ kcal mol^{-1}) colliding with C_2H_4 as 10–15 kcal mol^{-1}. Thus, the $C_2H_4F_2$ data are consistent with the other room-temperature studies. These three examples used different chemical activating reactions and different unimolecular reference reactions and were affected by different unwanted side reactions or other complications, yet they gave the same general result. Also similar average energy losses per collison have been reported for chemically activated C_2H_5F,[35]

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(33) M. Day and A. F. Trotman-Dickenson, *J. Chem. Soc., A*, 233, (1969).

(34) J. W. Simons, B. S. Rabonivotch, and D. W. Setser, *J. Chem. Phys.*, 41, 800 (1964).

although the data are not entirely self-consistent. Therefore, it seems that some confidence should be placed in the general magnitude found for the *average energy* transferred per collision; however, more accurate data at lower pressures are needed before the detailed form of the collision transition probabilities can be deduced for these highly vibrationally excited molecules.

Discussion

Chemical Activation Rate Constants for 1,2-$C_2H_4F_2$. A summary of rate constants for 1,2-$C_2H_4F_2$ formed by radical association at temperatures near 300 and 475° is given in Table II. The two investigations using photolysis of difluoroacetone are in good agreement with our work. The data from the photolysis of monofluoroacetone[4] gave rate constants that are too high and have a suspiciously small dependence upon temperature; rate constants for chemically activated C_2H_5F obtained in that study also seem to be in error.[32] Since the deactivation efficiency for these large acetone molecules should be greater than for CH_2ClF, which removes 11 ± 3 kcal mol^{-1} per collision, the CH_3COCH_2F data cannot be rationalized by assuming different collisional efficiencies. Since our measurements are over a wide range of pressures and since they are in good agreement with two other sets of data, we feel confident that these are the correct rate constants for 1,2-$C_2H_4F_2$* with an average energy of 92.5 and 95.2 kcal mol^{-1}.

Table II. Comparison of 1,2-$C_2H_4F_2$ Experimental Rate Constants

Radical source	Temp, °K	k_a/k_M, cm	k_a, sec^{-1}
$CH_2FCl + Hg(^3P_1)$	300	2.0 ± 0.1	2.0×10^8
	475	4.6 ± 0.2	$3.7\ (3.0)^a \times 10^8$
$(CH_2F)_2CO^b$	300	1.6	1.6×10^8
	475	3.6	$2.9\ (2.3)^3 \times 10^8$
$(CH_2F)_2CO^c$	300	2.2	2.2×10^8
	475	4.5	$3.6\ (2.9)^a \times 10^8$
$CH_3COCH_2F^d$	329	7.2^d	7.4×10^8
	470 ± 20	9.0	$7.7\ (6.2)^2 \times 10^8$

[a] The rate constant using a temperature-dependent collision diameter to calculate k_M. [b] Data from ref 5 with collision diameter of 5 Å for $(CH_2F)_2CO$. [c] The listed data from ref 3 at 300 and 324° were used to obtain the 300° rate constant. [d] Data from ref 4 with 5 Å for the collision diameter of CH_2FCOCH_3. The two low-temperature points of this study are not consistent with the other data, and extrapolation to 300° using all the data gave k_a/k_M = 5.2 cm.

Another interesting chemical activation system[5] for 1,2-$C_2H_4F_2$ is reaction 10. The reported k_a/k_M ratio

$$F_2 + C_2H_4F \longrightarrow 1,2\text{-}C_2H_4F_2^* + F$$
$$\Delta H_R^\circ = -69 \text{ kcal mol}^{-1} \quad (10)$$

was 5.5×10^{-4} cm which becomes $k_a = 5.4 \times 10^4$ sec^{-1} when multiplied by k_M. The magnitude of this rate constant corresponds to molecules with a total energy of about 67 kcal mol^{-1} according to the rate constants of Figure 3. The rate constant from chemically activated C_2H_5F formed by the reaction of ethyl radical with fluorine corresponds[15,32] to an energy of 69 kcal mol^{-1} which is a large share of the 71-kcal mol^{-1} enthalpy of the reaction. If the experimental data are correct, nearly all of the energy available to these fluorine abstraction reactions is partitioned to the molecule with the new C—F bond. The original investigators reached this conclusion too,[15] and it seems as if these reactions must occur on a highly attractive potential surface.[36] In fact these interesting reactions seem to be such extreme examples of attractive surfaces that further experimental investigation should be done to confirm the original measurements and to examine the distribution function of the formed vibrationally excited fluoroethanes.

Critical Energies for HF Elimination Reactions. The thermally activated HF elimination from C_2H_5F recently has been successfully studied,[33] and the Arrhenius parameters are log A = 13.31 ± 0.41 and E_a = 58.2 ± 1.3 kcal mol^{-1} (or an ϵ_0 of 56.7). Our RRKM analysis of the chemical activation data[32] for C_2H_5F gave $\epsilon_0 = 57$ kcal mol^{-1} in agreement with the other work.[15] This activation energy is 2–3 kcal higher than for C_2H_5Cl, which is in turn about 3 kcal higher than for C_2H_5Br. The value of 62 kcal mol^{-1} for 1,2-$C_2H_4F_2$ found in the present work is consistent with this trend, since higher ϵ_0 values have been suggested[11] as the reason that the chemically activated 1,2-haloalkanes have lower rate constants than the monohaloethanes at the same energy. The increase in the critical energy for HF elimination relative to HCl elimination can be explained by the extensively discussed polar transition state views of Maccoll.[37]

The chemical activation rate constants for 1,1-$C_2H_4F_2$, which were measured in two different systems by Kerr, O'Grady, and Trotman-Dickenson,[5a] are about equal to the C_2H_5F rate constants but are ten times higher than those for 1,2-$C_2H_4F_2$. The 1,1-$C_2H_4F_2$ results of Bryant and Pritchard[6] are in qualitative agreement with ref 8a, although the data are not as extensive. Evaluation of $E_{\min}$ (see Appendix) and calculation of k_ϵ curves using the same transition-state model as for 1,2-$C_2H_4F_2$ but the known frequencies for 1,1-$C_2H_4F_2$ gave $\epsilon_0 = 57$ kcal mol^{-1} for matching of experimental and calculated k_a values. This critical energy is essentially the same as for C_2H_5F. This result should perhaps be viewed with some caution since the ϵ_0 for 1,1-$C_2H_4Cl_2$ is about 3 kcal mol^{-1} lower[38] than for C_2H_5Cl. Also, it should be remembered that 1,1-haloethanes may eliminate HX by competitive α,α and α,β pathways.[27] The enhancement of the calculated rate for 1,1-$C_2H_4F_2$ over 1,2-$C_2H_4F_2$ is due to the higher frequencies of 1,1-$C_2H_4F_2$ which lowers the $N^*(\epsilon)$ term of eq I (roughly a factor of 3) and to the 5-kcal mol^{-1} higher ϵ_0 which contributes another factor of 3.

The deduction of useful thermochemical[13] values (ϵ_0 can be found for a known $\langle\epsilon\rangle$ or *vice versa*[39]) from measured chemical activation rate constants, when combined with RRKM calculations using reliable models

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(35) J. A. Kerr, B. V. O'Grady, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 275 (1969).

(36) P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, *J. Chem. Phys.*, **44**, 1168 (1966).

(37) A. Maccoll, *Chem. Rev.*, 69, 33 (1969).

(38) H. Hartmann, H. Heydtmann, and G. Rinck, *Z. Physik. Chem.* (Frankfurt), **28**, 71 (1961).

(39) This approach has been used for cyclopropane in various systems to assign ϵ: D. W. Setser and B. S Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962); J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964); R. J. Campbell and E. W. Schlag, *J. Am. Chem. Soc.*, **89**, 5103 (1967). Recent application also has been made to chemically activated methylcyclobutenes: C. S. Elliot and H. M. Frey, *Trans. Faraday Soc.*, **64**, 2352 (1968).

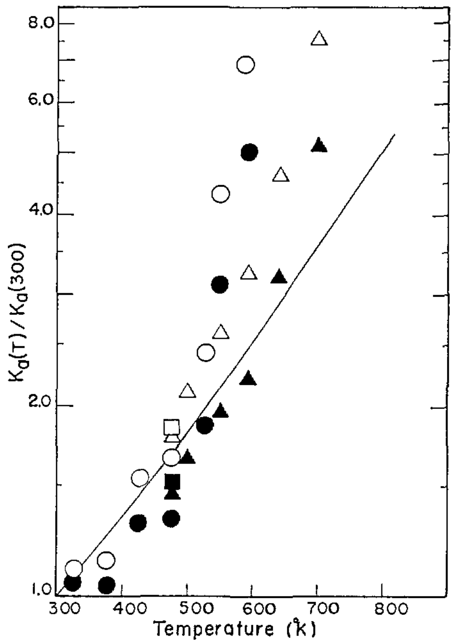

Figure 5. Comparison of calculated and experimental rate constants at various temperatures for 1,2-$C_2H_4F_2$: □, present work; ○, photolysis of $(CH_2F)_2CO$ (ref 3); △, photolysis of $(CH_2F)_2CO$ (ref 5). Open and closed symbols correspond to temperature-independent and -dependent cross sections. The line is the RRKM computed k_a^{∞} rate constants; at 200° the rate constant declines by 0.87 from the 300° value.

for a complex and molecule, has been deomonstrated here for 1,2-$C_2H_4F_2$ and elsewhere for C_2H_5F.[15,32] Classical RRK treatments of chemical activation data to obtain critical energies for various fluoroethanes have been done[3-7] following the general procedure of Benson and Haugen.[14] However, fitting the rate constant using the RRK approach requires values for $\langle\epsilon\rangle$, ϵ_0, and an uncertain empirical assignment for the number of critical oscillators. Some investigators also used an artificial collisional efficiency, which is equivalent to scaling the A factor of the classical equation, for converting the k_a/k_M experimental ratios to k_a values. The large difference between the critical energy for 1,1-$C_2H_4F_2$ and 1,2-$C_2H_4F_2$ emphasizes that attributing changes in rate constants to changes in the number of effective oscillators when certain features of the molecule are changed, for example, H atoms are replaced by heavier F or Cl atoms, without consideration of possible changes in ϵ_0, can be incorrect and is usually misleading. Values for ϵ_0 obtained by most workers[4,14] using the RRK formulation for C_2H_5F and 1,2-$C_2H_4F_2$ are similar (Trotman-Dickenson and coworkers[5] reported values of ~50 kcal mol^{-1} because they used larger values for s than Pritchard or Benson, but see ref 15 for a more recent interpretation) to ours from the RRKM calculations, but this is largely fortuitous due to cancellation of various factors. For example, Benson and Haugen used $\langle\epsilon\rangle = 85.4$, while we find 92.5 kcal mol^{-1} at 300°K, and they used a collisional inefficiency factor of 0.1–0.2, while we have shown that unit deactivation more nearly is appropriate. Pritchard and coworkers also used low values for the carbon–carbon bond dissociation energies of fluoroethanes, but the higher values selected in the Appendix now are favored.

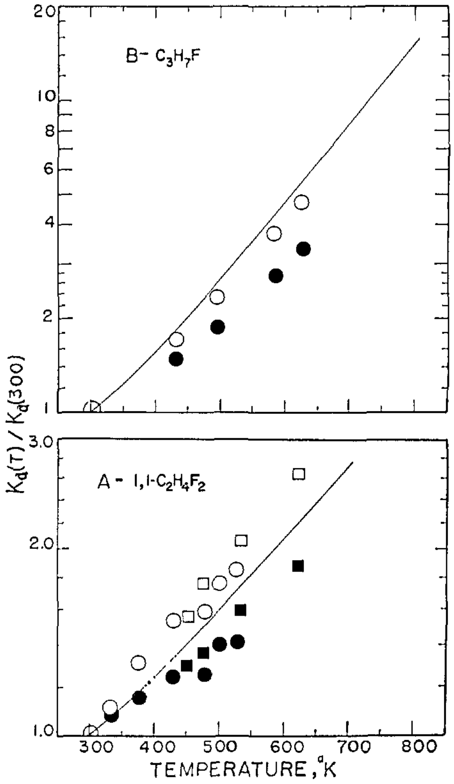

Figure 6. Comparison of calculated and experimental rate constants at various temperatures for (A) 1,1-$C_2H_4F_2$ (○, photolysis of CH_2CO with CH_2F_2; □, cophotolysis of acetones) and (B) n-C_3H_7F (cophotolysis of $(C_2H_5)_2CO$ and $(CH_2F)_2CO$). Open and closed symbols correspond to temperature-independent and -dependent cross sections. The lines are the calculated k_a^{∞} RRKM rate constants.

Temperature Dependence of Chemical Activation Rate Constants. For efficient deactivating gases with known collision diameters, the temperature dependence of the chemical activation rate constants is governed by the average energy of the reacting molecules. Comparison of calculated and experimental rate constants at various temperatures is one way to measure the dependence of k_ϵ upon energy. Extensive chemical activation data covering a wide range of temperature have been published for various fluoroalkanes and these results, in principle, constitute a test of the energy dependence of k_ϵ in the 95-kcal mol^{-1} region. The data for 1,2-$C_2H_4F_2$*, 1,1-$C_2H_4F_2$*, and n-C_3H_7F* will be examined with this objective in mind; however, the difficulty of selecting the correct collision diameters makes critical testing very difficult. The most quantitative verification of the energy dependence of the RRKM rate constants has been done with the butyl radical[39] in the 40-kcal mol^{-1} energy region.

For the fluoroalkanes $E_{\min} - \epsilon_0$ is large, so k_a does not depend strongly upon pressure even at the higher temperatures. However, some caution must be used for large molecules since calculations for unit deactivation gave $k_a^{\infty}/k_a^{0} = 2.0$ for n-C_3H_7F at 630°K. If an efficient but less than a unit deactivation mechanism is operating, this ratio will be reduced or even reversed (see Figure 4). Nearly all experiments used fluorinated ketones as the radical source. We already have shown that if the rate constants are measured with relatively efficient bath gases in the pressure region corresponding to linear D/S *vs.* $1/P$ plots, the experimental rate constants are nearly equivalent to the high-pressure RRKM calculated unit deactivation values, *i.e.*, $k_a^\infty = \langle k_\epsilon \rangle$. Comparison of experimental and calculated results will be made with a $k_a^\infty(T)/k_a^\infty(300)$ *vs.* T(°K) plot. The main reason for this is that, although the different sets of data may not exactly agree in regard to absolute values for the rate constants, the temperature dependence should be consistent from one laboratory to another. The experimental rate constants are defined as $k_a = [P_M]k_M(D/S)$. Fortunately the actual experimental D/S values at a particular pressure are usually reported, and it only is necessary to choose the appropriate collision diameters to evaluate $k_M(T)/k_M(300)$, and hence $k_a^\infty(T)/k_a^\infty(300)$. The collision diameter does not enter into the RRKM $\langle k_\epsilon \rangle$ value. The temperature dependence of *collisional stabilization* diameters is not known, and the data were treated to display two possibilities. Use of temperature-independent diameters gave the open symbols of Figures 5 and 6; the ratio, $k_M(T)/k_M(300)$, simply varies as $(300/T)^{1/2}$. The filled points were obtained by using the reduced Ω^* integrals with $\epsilon/k = 400°$ to modify the cross section with temperature; $k_M(T)/k_M(300)$ becomes $[\Omega^{*2,2}(T)/\Omega^{*2,2}(300)]\,(300/T)^{1/2}$. The difference between the experimental rate constants calculated in these two ways is significant and, in fact, the Ω^* integral ratio declined from unity to 0.7 at 600°K.

The calculated results will be considered first. The vibrational frequencies of n-C_3H_7F are available, and the activated complex model was a straightforward extension (replacement of H by CH_3) of the C_2H_5F complex model.[32] We used an E_{min} of 83.9 kcal (see Appendix) and the same ϵ_0 as for C_2H_5F. The models gave a thermal activation rate constant of $10^{13.3}$ exp[$-(57{,}000/RT)$]. The calculated 300°K chemical activation rate constant was $k_a^\infty = 4.3 \times 10^6$ sec^{-1} compared to the experimental value[35] of 9×10^6 sec^{-1} measured in the cophotolysis of $(C_2H_5)_2CO$ and $(CH_2F)_2CO$ ($k_a/k_M = 1.0$ mm). Considering the uncertainty in the values chosen for ϵ_0, E_{min}, and collision diameters, this is adequate agreement. This extension of the calculations to n-C_3H_7F illustrates the usefulness of the RRKM theory when used in the appropriate way with reliable models. It is interesting that the RRKM rate constants gave a virtually linear log k_a *vs.* T plot for $C_2H_4F_2$ and C_3H_7F. This is the case because, for small ranges of energy, k_ϵ varies as some constant power of the total energy in the molecule. Since the energy is nearly a linear function of temperature for the range studied, log k_a is linear with temperature. The same distribution function was used for both 1,1-$C_2H_4F_2$ and 1,2-$C_2H_4F_2$; therefore, the slightly greater temperature dependence of the calculated rate constants for 1,2-$C_2H_4F_2$ arises from the steeper dependence of k_ϵ upon energy for 1,2-$C_2H_4F_2$ than for 1,1-$C_2H_4F_2$. The origin of this effect is the lower frequencies of the 1,2-$C_2H_4F_2$ molecule. The k_a^∞ values for C_3H_7F vary much more strongly with temperature than for either $C_2H_4F_2$ molecule. This is due to the greater dependence of k_a upon energy, which is characteristic of larger molecules, and also to the greater increase in average thermal energy of C_3H_7F with temperature; *e.g.*, the thermal energies are 2.9 and 3.1 kcal mol^{-1} at 300° and 8.0 and 9.4 kcal mol^{-1} at 600° for $C_2H_4F_2$ and C_3H_7F, respectively.

Consider next a comparison of the experimental and calculated temperature dependence of the rate constants shown in Figures 5 and 6. The first conclusion is that the rate constants for 1,2-$C_2H_4F_2$ above 550° increase much too rapidly and are unreliable. The experimental results for 1,1-$C_2H_4F_2$ and n-C_3H_7F seem well behaved over the temperature range that is plotted. For the $C_2H_4F_2$ cases, Figures 5 and 6a, reasonable agreement is found between the calculated rate constants and either set of the experimental rate constants. The large scale of these two plots should be noted, and, in fact, most points are within 20% of the calculated results. These data can be taken as general support for the energy dependence predicted by eq I. The use of the temperature-dependent cross section enhances the agreement for the 1,2-$C_2H_4F_2$ higher temperature points but lessens the agreement at lower temperatures. For 1,1-$C_2H_4F_2$ the calculated results lie almost exactly between the two sets of experimental rate constants. The n-C_3H_7F data seem to unequivocally favor the temperature-independent cross sections for which there is good agreement with the calculated results. Before a firm general conclusion can be reached, more carefully designed experiments need to be done which cover a wider temperature range with direct measurement of k_a^∞ using bath gases with known deactivation mechanisms, *i.e.*, a measured or known $\langle \Delta E \rangle$ per collision for each temperature. It is important to recognize that low temperatures are as useful as high ones for this purpose. Although any conclusion is premature, the data may favor a less temperature-dependent cross section than that given by the Ω^* integral with an ϵ/k of 400°.

The temperature dependence of the fluoroalkane chemical activation rate constants has been previously treated using the classical Kassel equation as suggested by Benson and Haugen.

$$k_a = k_{\langle\epsilon\rangle} = A\left[\frac{E_{min} + \langle\epsilon\rangle_{th} - \epsilon_0}{E_{min} + \langle\epsilon\rangle_{th}}\right]^{s-1} \qquad \text{(IV)}$$

The effect of temperature was estimated by calculating the average thermal energy, $\langle\epsilon\rangle_{th}$, carried into the active degrees of freedom of the molecule by the combining radicals. It was assumed that three translational, three rotational, and all vibrational degrees of freedom of the radicals contributed to $\langle\epsilon\rangle_{th}$. This method gave higher values than the distribution function of eq III. For example, $\langle\epsilon\rangle_{550} - \langle\epsilon\rangle_{300}$ for 1,2-$C_2H_4F_2$ was 6.9 kcal mol^{-1} according to Benson and Haugen but is only 4.2 kcal mol^{-1} when calculated from f(ϵ). The log of the right-hand side of (IV) can be expanded in terms of $(E_{min} - \epsilon_0 + \langle\epsilon\rangle_{th})/\epsilon_0$. If $\langle\epsilon\rangle_{th}$ is approximately a linear function of temperature (as it nearly is for $C_2H_4F_2$ and C_3H_7F from 300 to 600°K), it can be shown that according to eq IV the log plot of $k\langle\epsilon\rangle$ *vs.* temperature should be linear with slope equal to $(s - 1)$. Such plots of chemical activation rate constants have been used to assign the number of effective oscillators for a variety of the fluoroalkanes. There are several other ways[40] of defining the number of critical oscillators depending upon what properties are being described, *e.g.*, thermal unimolecular fall-off data or some average energy quantity. The method just mentioned using eq IV is based mainly upon fitting the energy dependence of k_ϵ at energies slightly above E_{min}. In this method some con-

(40) D. W. Placzek, B. S. Rabinovitch, G. Z. Whitten, and E. Tschuikow-Roux, *J. Chem. Phys.*, **43**, 4071 (1965).

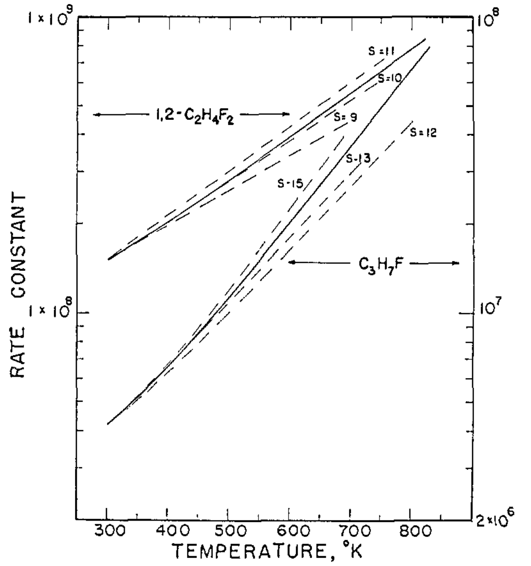

Figure 7. A comparison of the RRK rate constants (dotted lines) to the RRKM values (solid lines) as a function of temperature. The RRKM values are the k_a^∞ rate constants calculated according to eq II with E_{min} = 89.6 and ϵ_0 = 62 kcal mol^{-1} for 1,2-$C_2H_4F_2$, and E_{min} = 83.9 and ϵ_0 = 57 kcal mol^{-1} for n-C_3H_7F.

sideration may be given to the absolute value of k_a in selection of best values for s, but mainly the absolute value was controlled by use of ϵ_0 and the collisional inefficiency factor (this is not justifiable for most polyatomic bath gases) as variable parameters. It should be explicitly noted that for this use of eq IV, the thermal energy, $\langle\epsilon\rangle_{th}$, was not evaluated by classical statistical arguments. In fact, the number of effective oscillators needed to describe falloff data or average energies of reacting 1,2-$C_2H_4F_2$ molecules under thermal activation conditions was calculated to be considerably smaller (~7 at 800°K) than the value of s needed to fit the energy dependence of eq IV.

Comparison of the RRKM and RRK rate constants on a log k_a *vs.* temperature plot for 1,2-$C_2H_4F_2$ is shown in Figure 7. The RRK values were computed using E_{min} = 89.6 and ϵ_0 = 62 kcal mol^{-1}; the average energy was evaluated from the RRKM distribution function. The constant A of eq IV was arbitrarily adjusted to fit the RRKM result at 300°; the required value was $10^{12.52}$ sec^{-1} for s = 10 which gave the best fit to the RRKM curve. A single value of s gives reasonably good fit from 300 to 700°K which covers an energy range from 92.5 to 99.7 kcal mol^{-1}. If a similar plot for 1,2-$C_2H_4F_2$ is made for a hypothetical chemical activation system with the same ϵ_0 and f(ϵ), but with E_{min} = 75 and 67 kcal mol^{-1}, the values of s necessary to fit the RRKM results are 7.6 and 5.5, respectively.

A graph similar to Figure 7 was constructed[32] for CH_3CH_2F. A value of s equal to 10 gave the best agreement with the RRKM results. For this type of assignment the increase in s for 1,2-$C_2H_4F_2$ relative to C_2H_5F was less than 0.5. The effect of the number of degrees of freedom upon these plots was investigated by comparing the RRK and RRKM calculated results for C_3H_7F. Figure 7 shows that the RRKM results form a less linear plot than before; as would be expected, s increased relative to 1,2-$C_2H_4F_2$ and a value of 14 gave good agreement with the RRKM curve up to ~700°K. The A factor needed to match the 300°K rate constants was $10^{12.63}$ sec^{-1}. It should be recognized that these A factors are an order of magnitude lower than the measured Arrhenius preexponential factors for these HX elimination reactions. This is not surprising since they were utilized as empirical parameters.

For quantitative interpretation of the temperature dependence of chemical activation rate constants, it may be concluded that the RRKM form of k_ϵ should be combined with a well-defined representation of the distribution function of the activated molecules. Furthermore, careful attention should be given to establishing the deactivation model and the possible temperature dependence of collision cross sections.

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Appendix

Summary of Thermochemistry

The desired energy quantity is E_{min} of the chemically activated fluoroalkanes, which is the carbon–carbon bond dissociation energy at 0°K plus the activation energy for combining reactions (assumed to be 1 kcal mol^{-1}). In most cases the bond dissociation energies have not been directly measured, and the best procedure is to combine $\Delta H_f{}^\circ{}_0$(R–R′) with $\Delta H_f{}^\circ{}_0$(R) and $\Delta H_f{}^\circ{}_0$(R′), which can be obtained by selecting the "best" measurements of D°(R–H). In general the enthalpy of formation of the fluorinated methanes are known, and we have used the recently published tabulation by Lacher and Skinner[41] which is based upon the revised $\Delta H_f{}^\circ$(HF,aq). The thermochemical values are summarized in Table III; C_2H_5Cl and 1,2-$C_2H_4F_2$ were included only for comparison.

The $\Delta H_f{}^\circ{}_{298}$ for C_2H_6, CH_3CF_3, and CH_3CHF_2 are available, and these values were merely converted to 0°K. Unfortunately the $\Delta H_f{}^\circ$(C_2H_5F) and $\Delta H_f{}^\circ$(1,2-$C_2H_4F_2$) have not been reported. Bernstein's group additivity tables,[42] which give the correct $\Delta H_f{}^\circ$ for C_2H_5Cl, lead to $\Delta H_f{}^\circ{}_{298}$($C_2H_5F$) = −63 kcal mol^{-1}. This gives $D_0{}^\circ$(C_2H_5–F) = 105.8, which is similar to $D_0{}^\circ$(CH_3–F) = 106.8 kcal mol^{-1} and supports the assignment. Bernstein's method gives $\Delta H_f{}^\circ$(1,2-$C_2H_4F_2$) as −106 kcal mol^{-1} at 298°. Lacher and Skinner considered enthalpy changes for redistribution reactions such as $^1/_2$(C_2H_6 + CH_2F–CH_2F) → C_2H_5F. These reactions seem to be nearly thermoneutral and $\Delta H_f{}^\circ$($C_2H_4F_2$) = −106, if $\Delta H_f{}^\circ$(C_2H_5F) = −63 kcal mol^{-1} is used.

The bond dissociation energy for methane[43] is firmly established as 104 ± 1 kcal mole^{-1}. Whittle and coworkers[44] studied D(CH_2F–H) and D(CHF_2–H) in competitive bromination reactions at 200° and estimated that both had C–H bond energies of 101 kcal mol^{-1} at

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(41) J. R. Lacher and H. A. Skinner, *J. Chem. Soc., A*, 1034 (1968).

(42) H. J. Bernstein, *J. Phys. Chem.*, 69, 1550 (1965).

(43) D. M. Golden and S. W. Benson, *Chem. Rev.*, 69, 125 (1969).

(44) A. M. Tarr, J. W. Coomber, and E. Whittle, *Trans. Faraday Soc.*, 61, 1182 (1965).

Table III. Thermochemical Values (kcal mol^{-1})

R	D(R–H)[a]	$\Delta H_f°_0$(R–H)[b]	$\Delta H_f°_0$(R)[b]	$\Delta H_f°_0$(R–R′)[b]	E_{min}(R–R′)[c]	R′
CH_3	104 ± 1[d]	−16.0[h]	34.9	−16.5	87.3	CH_3
CH_2F	101[e]	−53.9[i]	−7.1	−59.4[j]	88.2	CH_3
CH_2F	101[e]	−53.9[i]	−7.1	−102.8[j]	89.6	CH_2F
CHF_2	101[e]	−106.4[i]	−59.3	−114.6[i]	91.2	CH_3
CF_3	106 ± 1[f]	−165.0[i]	−112.1	−175.1[i]	98.9	CH_3
CF_3	106 ± 1[f]	−165.0[e]	−112.1	−319.0[i]	95.8	CF_3
CH_2Cl	100[g]	28.7[g]	28.7[g]	−23.2[g]	87.8[g]	CH_3
CH_2Cl	100[g]	28.7[g]	28.7[g]	−26.9[g]	85.3[g]	CH_2Cl

[a] These are experimental values reported at 298°K unless specified otherwise. We have assumed that these values are bond dissociation enthalpies and made our corrections to 0°K accordingly. [b] Tabulated for 0°K. [c] $E_{min} = D°(R–R^1)$ at 0°K plus 1 kcal mol^{-1}. [d] See ref 43. [e] Measured at 200° by ref 44; see text for justification. Error limits are larger than for $D(CH_3–H)$ and $D(CF_3–H)$. [f] See ref 45. [g] See ref 10 and 11. The E_{min} values for C_2H_5Cl and $C_2H_4Cl_2$ differ by 0.6 kcal mol^{-1} from our earlier work because the conversion to 0° was done in a slightly different way. [h] JANAF Thermochemical Tables. [i] See ref 41; these values are based upon the revised ΔH_f(HF,aq). [j] See text of Appendix.

200°. Comparison of the activation energies[19] for H abstraction by CF_3 also indicates the bond dissociation energies of CH_3F and CH_2F_2 to be nearly equal and perhaps slightly higher than for CH_3Cl. Bromination studies of fluoroalkanes[45] seem reliable and indicate the $D(CH_2F–H)$ to be less than $D(CH_3–H)$ or $D(CF_3–H)$. An additional reservation arises because $\Delta H_f°(CH_3F)$ has not been accurately measured, although Lacher and Skinner seem to be confident of −55.9 kcal mol^{-1} at 298°K.

The $\Delta H_f(CF_3)$ seems firmly established due to the measurements of Amphlett and Whittle[45] of $D°(CF_3–H)$ = 106.7 ± 0.5 kcal mol^{-1}. Such a value leads to quite high energies for bonds attached to CF_3. However, recent measurements[3b] of chemical activation rate constants for $CH_3CH_2CF_3$ activated by $CH_3 + CH_2CF_3$ and $CF_3 + CH_2CH_3$ also support a difference of approximately 4.5 kcal mol^{-1} between two carbon–carbon bonds.[46]

The E_{min} for n-C_3H_7F formed by association of C_2H_5 and CH_2F was taken as 83.9 kcal mol^{-1}. This follows from $\Delta H_f°_{298}(C_3H_7F)^{41} = -67$ kcal mol^{-1}, the value for $\Delta H_f°(CH_2F)$ in Table III, and the usual $\Delta H_f°(C_2H_5)$ based upon $D°(C_2H_5–H)$ of 98 kcal mol^{-1}.

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(45) J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, **64**, 2130 (1968).

(46) On the other hand recent mass spectrometer work (T. C. Ehlert, *J. Phys. Chem.*, **73**, 949 (1969)) favors $\Delta H_f°_{298}(CF_3) = 102.5 \pm 3$ kcal mol^{-1}.

Transannular Dipolar and Neighboring Group Effects in Simple Oxygen Heterocycles on Rates of Solvolysis of Arenesulfonates[1]

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Abstract: The rate of acetolysis of the following arenesulfonates has been studied at 85°: 4-tetrahydropyranyl (**1b**, **1d**), 3-tetrahydropyranyl (**2b**), 4-tetrahydrothiopyranyl (**3b**), 1-methoxy-3-pentyl (**4b**), 1,5-dimethoxy-3-pentyl (**5b**), and 3-tetrahydrofuranyl (**6b**). All of the heterocyclic compounds showed substantial rate reductions, compared to the open-chain methoxy compounds **4b**, **5b**, and cyclohexyl and cyclopentyl arenesulfonates. The rate retardation is attributed to a transannular dipolar field effect exerted by the heterocyclic oxygen atom. This explanation is supported by measurement of the carbonyl stretching frequency of the related ketones, **1c**, **2c**, **6c**, 2- and 4-methoxycyclohexanones, cyclohexanone, and cyclopentanone. Within the series of arenesulfonates studied, 3-tetrahydropyranyl brosylate solvolyzed much faster than predicted, in spite of the rate-retarding dipolar effect. This relatively rapid rate is attributed to the promoting effect on the solvolysis of 1,3-transannular oxygen participation, which has not been noted before. Such participation is not important with the 4-tetrahydropyranyl or the 3-tetrahydrofuranyl compounds for reasons of strain.

It is well known that methoxyl groups can assist solvolysis and displacement reactions through intermediate formation of methoxonium ions.[2] This phenomenon, in which we became interested[3,4] during some structural studies on natural products, is examined in the present paper by studying rates of solvolysis of arenesulfonates in which the ether oxygen affecting sol-

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(1) In memory of Winston Danae Walters: "And gladly wolde he lerne, and gladly teche."

(2) (a) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958); (b) E. Allred and S. Winstein, *J. Am. Chem. Soc.*, 89, 3991 (1967); 89, 3998, 4008, 4012 (1967).

(3) D. S. Tarbell, *et al.*, *ibid.*, **83**, 3096 (1961).

(4) (a) E. R. Novak and D. S. Tarbell, *ibid.*, **89**, 73 (1967); (b) A. W. Friederang and D. S. Tarbell, *J. Org. Chem.*, **33**, 3797 (1968); (c) J. R. Hazen, and D. S. Tarbell, *Tetrahedron Lett.*, 5927 (1968); (d) J. R. Hazen, *ibid.*, 1897 (1969); R. J. Gargiulo and D. S. Tarbell, *Proc. Nat. Acad. Sci. U. S.*, 62, 52 (1969).