The Decomposition of Vibrationally Excited 1,1,1-Trideuterio-2,2-difluoroethane[1]

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Abstract: Evidence is presented that the vibrationally "hot" molecule $CF_2HCD_3^*$, formed by the combination of CF_2H and CD_3 radicals, may decompose by three competing unimolecular processes to form $CFH{=}CD_2 + DF$, $CFD{=}CD_2 + HF$, and $CF_2{=}CD_2 + HD$. The second process, a three-center α,α elimination of HF from the same carbon atom, has not previously been observed. The evidence for the third process, HD elimination, is more tentative. An estimation of the Arrhenius parameters for the decompositions using classical Rice–Ramsperger–Kassel (RRK) theory is made, and the effect of collisional quenching of the "hot" molecules is discussed in terms of the critical energies for the eliminations. A similar experiment with $CFH_2CD_3^*$ showed no α,α elimination of HF.

The dehydrohalogenation of haloethanes is generally accepted to proceed *via* a four-center transition state (α,β elimination) in both thermal[2] and chemical activation[3] systems. However, in some preliminary experiments on the vibrationally "hot" molecule $CF_2HCD_3^*$, formed by the chemical activation technique,[4] we observed the formation of both d_3- and d_2-vinyl fluoride, leading us to suggest that a three-center elimination may occur in which both the hydrogen and halogen atom come from the same carbon atom, α,α elimination.[5] We have observed[5,6] that our interpretation of the elimination of HF from the "hot" molecules $CF_2HCFH_2^*$ and $CF_2HCF_2H^*$ may be complicated by the occurrence of such a process.

Herein we give a detailed report of the decomposition of the "hot" $CF_2HCD_3^*$ molecule.

Experimental Section

Mixtures of chromatographically pure 1,1,3,3-tetrafluoroacetone (TFA) and d_6-acetone (d_6A), which was 99.5% D, were photolyzed together in the 3130-Å region. Experiments were generally conducted on a mercury and grease-free apparatus at low pressures[6] and on a convential apparatus[7] at higher pressures. None of our reported products can be due to Hg-sensitized processes. Product identification and analysis was performed by vpc and mass spectrometry. The methanes and ethane CF_2H_2, CF_2HD, and C_2D_6 were observed but no analysis was carried out.[8] The following ethanes and ethylenes were identified: CF_2HCD_3, CF_2HCF_2H, $CFH{=}CD_2$, $CFD{=}CD_2$, and $CF_2{=}CD_2$. At small percentage conversions no other volatile products were observed. Vpc calibrations for the deuterated products were made with their nondeuterated analogs. The vinyl fluoride peak was collected off the chromatograph in each experiment and the ratio of d_3- to d_2-vinyl fluoride was determined by the 49/48 parent mass ratio on the mass spectrometer. The mass spectra of each of the product fractions were compared carefully with standard samples of CF_2HCH_3, CF_2HCF_2H, $CFH{=}CH_2$, and $CF_2{=}CH_2$, and the identification and deuterium composition of the products that we report are unequivocal.[9] The major peaks in the mass spectrum of CF_2HCD_3 were at *m/e* 51 (base peak), 69 (parent), and 50 in the ratio of 1:0.5:0.15. The probable positive ions are CF_2H^+, $CF_2HCD_3^+$, and $CFHCD_3^+$ (the CF_2^+ ion peak, which is also at *m/e* 50, is negligible in the mass spectrum of CF_2HCH_3). Small ion peaks, ~1% of the base peak, occurred at *m/e* 52 (after C^{13} isotope correction), 35, and 34; the probable ions are CF_2D^+, CFD_2^+, and $CFHD^+$, respectively, and may be assumed to be rearrangement (transference) peaks. If the contribution from the $CF_2CD_3^+$ ion was assumed to be zero, the sample possibly contained a maximum of <2.5% CF_2HCD_2H (this compound may be expected since there was a 3% d_5 impurity in the d_6A).

Blank experiments were run to ensure that there was no isotopic exchange between the ketones in the reaction vessel and between the d_6A and fluoroethylenes on the vpc column; *e.g.*, no deuterium substitution occurred when a sample of $CFH{=}CH_2$ and d_6A was run on the column under our analytical conditions.

Some experiments were carried out under similar conditions over the same temperature range with chromatographically pure 1,3-difluoroacetone (DFA) and d_6A. Analysis of the ethylene fraction indicated only the production of $CH_2{=}CD_2$ as shown by the parent peak at *m/e* 30 in the mass spectrum; after C^{13} isotope correction, no $CHD{=}CD_2$ was evident in the spectrum.

A series of experiments was also conducted with TFA and d_6A mixtures in the presence of varying pressures of perfluorocyclohexane as an added gas, and a few experiments with added N_2 were performed.

Results and Discussion

Some typical data are given in Table I, mainly consisting of runs done at total pressure of 40 mm of ketone (30 mm of d_6A + 10 mm of TFA). In many of these experiments varying pressures of $c\text{-}C_6F_{12}$ were added.

Other series of runs were carried out at 0.4–0.5 and 21–23 mm total pressure and some individual experiments at several different pressures. In these experiments, the d_6A/TFA ratio was usually about 2, and only analysis for vinyl fluoride was carried out. Representative data with no added gases are shown as a function of the 49/48 mass ratio *vs.* temperature in Figure 1. It is seen that the 49/48 ratio tends to a value of just less than 0.5 at higher temperatures, independent of the total ketone pressure. At lower temperature greater 49/48 ratios are obtained at lower total pressure. One experiment at 229° and 20 mm pressure was carried out with the incident light intensity reduced by a factor of 20 with a 3130-Å interference filter, but no change in the 49/48 ratio was observed.

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[1] This work was supported by a grant from the National Science Foundation, GP-4090.

[2] See H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967), for a very recent review.

[3] J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, **45**, 3246 (1966); R. L. Johnson and D. W. Setser, *J. Phys. Chem.*, **71**, 4366 (1967).

[4] B. S. Ravinovitch and M. C. Flowers, *Quart. Rev.* (London), **18**, 122 (1964).

[5] J. T. Bryant, B. Kirtman, and G. O. Pritchard, *J. Phys. Chem.*, **71**, 1960 (1967).

[6] G. O. Pritchard and J. T. Bryant, *ibid.*, **72**, 1603 (1968).

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

[8] The fraction volatile at −195°, CO, CD_3H, and CD_4, was not analyzed.

[9] J. T. Bryant, Ph.D. Thesis, University of California at Santa Barbara, 1967.

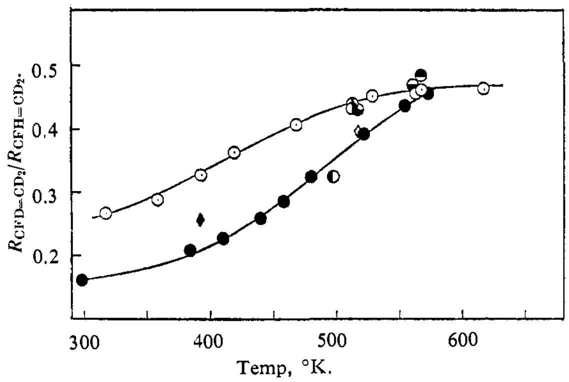

Figure 1. Plot of $R_{CFD=CD_2}/R_{CFH=CD_2}$ (49/48 ratio) *vs.* temperature for different ketone pressures: ⊙, 0.4–0.5 mm, d$_6$A/TFA = 2, lps; ●, 40 mm, d$_6$A/TFA = 3, hps; ⦶, 5 mm, d$_6$A/TFA = 3, lps; ◒, 10 mm, d$_6$A/TFA = 2, lps; ◓, 20 mm; ◑, 20 mm, two coincident results, one with incident intensity reduced by a factor of 20, d$_6$A/TFA = 9, lps; ◇, 20 mm, d$_6$A/TFA = 2, hps; ◆, 15 mm, d$_6$A/TFA = 6.5, lps; ◐, 80 mm, d$_6$A/TFA = 3, lps. lps and hps are low- and high-pressure systems, respectively. The last two results show that the pressure effect is not an artifact of changing the apparatus.

The Vinyl Fluorides. To explain the observed products we propose the following reaction sequence

$$\mathrm{CF_2H + CD_3 \longrightarrow CF_2HCD_3^* \xrightarrow{M} CF_2HCD_3} \qquad \text{(1a)}$$

$$\mathrm{CF_2HCD_3^* \longrightarrow CFD{=}CD_2 + HF} \qquad \text{(1b)}$$

$$\mathrm{CF_2HCD_3^* \longrightarrow CFH{=}CD_2 + DF} \qquad \text{(1c)}$$

where M is a quenching molecule. All of the other observed products, CF_2HCF_2H, C_2D_6, CF_2H_2, etc., are readily accountable for by well-established radical–radical and radical–molecule interactions, except for the $CF_2{=}CD_2$; discussion of this product is given later in the paper.

Although reactions 1a and 1c are readily acceptable as sources of CF_2HCD_3 and $CFH{=}CD_2$, reaction 1b requires further justification. The positive identification of CF_2HCD_3 as the *only* deuteriofluoroethane in the system shows that *no* other "hot" ethane[10] can be a source of the d_3-vinyl fluoride including the possible rearrangement of the "hot" molecule in reaction sequence 1 before dehydrofluorination occurs.

The mechanism predicts that the rate of elimination from the "hot" molecule should approach zero at infinite pressure,[11] which may be demonstrated by making the plots given in Figure 2. These are given for the total elimination and for $R_{CFD=CD_2}$ (R = rate of formation) at two different temperatures. The experiments shown are for a constant pressure of the ketones with a varying pressure of c-C_6F_{12} (see Table I). Because the three molecules will have differing deactivating efficiencies, the equations used are

$$\frac{R_{(CFD=CD_2\,+\,CFH=CD_2)}}{R_{CF_2HCD_3}} = \frac{k_{1b} + k_{1c}}{k_{1a}[\mathrm{TFA}] + k_{1a}'[\mathrm{d_6A}] + k_{1a}''[c\text{-}\mathrm{C_6F_{12}}]} \qquad (2)$$

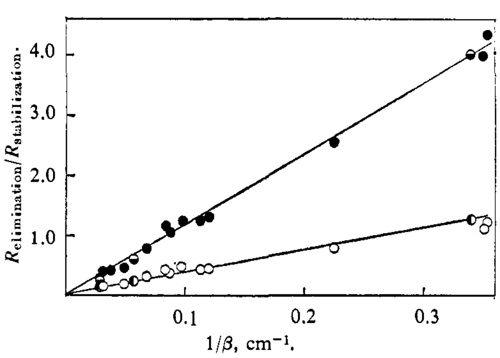

Figure 2. Plot of $R_{elimination}/R_{stabilization}$ *vs.* reciprocal pressure. $\beta = P_{TFA} + 0.61P_{d_6A} + 1.45\,P_{c\text{-}C_6F_{12}}$ cm: ● and ◒, $R_{(CFD=CD_2\,+\,CFH=CD_2)}/R_{CF_2HCD_3}$ at 240–247° and 300°, respectively; ○ and ◐, $R_{(CFD=CD_2}/R_{CF_2HCD_3}$ at 240–247 and 300°, respectively.

and

$$\frac{R_{CFD=CD_2}}{R_{CF_2HCD_3}} = \frac{k_{1b}}{k_{1a}[\mathrm{TFA}] + k_{1a}'[\mathrm{d_6A}] + k_{1a}''[c\text{-}\mathrm{C_6F_{12}}]} \qquad (3)$$

An equation of this form was originally tested by Giles and Whittle[12] for the deactivation of $CF_3CH_3^*$ formed in the cophotolysis of acetone (A) and hexafluoroacetone (HFA). Since deactivation is by collision, k_{1a} etc. may be replaced by QZ etc., where $Q \leq 1$. Using the relative values of Q given[12] for HFA, A, and c-C_6F_{12}, $Q = 0.75$, $Q' = 0.39$, and $Q'' = 1.0$, and, assuming that HFA ≡ TFA and A ≡ d$_6$A, eq 3, for example, becomes

$$\frac{R_{CFD=CD_2}}{R_{CF_2HCD_3}} = \frac{k_{1b}}{k_{1a}\{[\mathrm{TFA}] + 0.61[\mathrm{d_6A}] + 1.45[c\text{-}\mathrm{C_6F_{12}}]\}} \qquad (4)$$

This equation and the one corresponding to (2), both in pressure units, are tested in Figure 2. It is evident that the "hot" molecule mechanism for the formation of both of the vinyl fluorides is satisfactorily established. Reaction 1b presumably proceeds *via* the intermediate $\ddot{C}F\text{–}CD_3$, which then rearranges, or the deuterium atom migration may occur simultaneously with the three-center α,α elimination.

As indicated by our experiments it is seen that only an α,β process occurs in the reaction sequence

$$\mathrm{CFH_2 + CD_3 \longrightarrow CFH_2CD_3^* \longrightarrow CH_2{=}CD_2 + HF} \qquad (5)$$

This observation parallels that of Tang and Rowland[13] who in recoil tritium experiments with the molecules CD_3CH_2Cl, CH_3CD_2F, and CD_3CH_2F found only an α,β-elimination process. It would seem that two fluorine atoms on the same carbon atom are necessary for the α,α process. HF elimination occurs from the excited molecule $CHTF_2^*$,[14] and the decomposition of CF_3H into CF_2 and HF in shock tubes has been studied;[15] the minimum energy for the dissociation (E^* in the RRK equation, see later) was calculated to be between 58[15a] and 69[15b] kcal mole^{-1}. It has also been demonstrated

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[10] *E.g.*, one could postulate that $CF_2DCD_2H^*$ may be formed *via* the reaction sequence $2CF_2H \rightarrow CF_2 + CF_2H_2$ followed by the interaction of CF_2 with CD_3H.

[11] J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, **45**, 3237 (1966).

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

[13] Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 570 (1968).

[14] Y.-N. Tang and F. S. Rowland, *ibid.*, **88**, 626 (1966).

[15] (a) A. P. Modica and J. E. LaGraff, *J. Chem. Phys.*, **44**, 3375 (1966); (b) E. Tschuikow-Roux and J. E. Marte, *ibid.*, **42**, 2049 (1965).

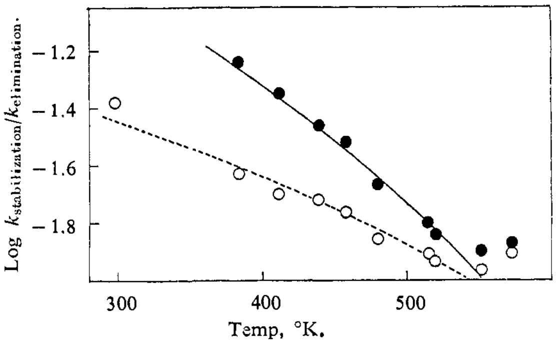

Figure 3. Comparison of observed and theoretical temperature dependence: ●, log k_{1a}/k_{1b}; ○, log k_{1a}/k_{1c}; ———, RRK plot, n = 12, $E_{\alpha,\alpha}^* = 64$ kcal mole^{-1}, log $(QZ/A_{\alpha,\alpha} = -7.29$; ----, RRK plot, n = 12, $E_{\alpha,\beta}^* = 53$ kcal mole^{-1}, log $(QZ/A_{\alpha,\beta}) = -6.09$. For convenience, both the theoretical and experimental values of log k_{1a}/k_{1b} have been shifted by −0.3.

that elimination of molecular hydrogen in the vacuum uv photolysis of CH_3CD_3 is mainly an α,α process.[16]

Benson and Haugen[17] and we, in subsequent publications,[6,18] have treated the decomposition of several "hot" fluoroethanes using RRK theory; in this case we have

$$k_{1b} = A_{\alpha\alpha}\left(1 - \frac{E_{\alpha\alpha}^*}{E}\right)^{n-1} \qquad (6)$$

and

$$k_{1c} = A_{\alpha\beta}\left(1 - \frac{E_{\alpha\beta}^*}{E}\right)^{n-1} \qquad (7)$$

The number of effective oscillators, n, is assumed to be the same for both eliminations, and a value of n = 12 has been adopted[17,18] for the comparison of experimental and theoretical data, relative to collisional deactivation, which is given in Figure 3. The internal energy, E, was taken to vary between 85.4 kcal mole^{-1} at 298°K and 92.7 kcal mole^{-1} at 560°K. The curve fitting yields values of $E_{\alpha\beta}^* = 53$ kcal mole^{-1} and $E_{\alpha\alpha}^* = 64$ kcal mole^{-1}.[19] The latter value lies in the range found for the HF elimination from CF_3H.[15] The ratios $QZ/A_{\alpha\alpha}$ and $QZ/A_{\alpha\beta}$ lead to values of $Q(\alpha,\alpha) = 0.16$ and $Q(\alpha,\beta) = 2.6$ for the composite bath gas, based on assumed A factors of $10^{13.5}$ sec^{-1} and $Z = 10^7$ collisions mm^{-1} sec^{-1}. A quenching efficiency of greater than unity is not meaningful; however, if $A_{\alpha\beta} = 10^{13.1}$ sec^{-1} is adopted, $Q(\alpha,\beta)$ becomes unity. This type of result is typical of the application of the simple RRK theory to these systems, and the comparison between the theoretical model and the experimental system is quite reasonable; obviously a better correspondence between $Q(\alpha,\alpha)$ and $Q(\alpha,\beta)$ may be obtained by assuming a slightly higher A factor for the three-center elimination.

Using the values given above in eq 6 and 7, we find that k_{1b}/k_{1c} shows about a 2.5-fold increase between 298 and 560°K, which is the type of behavior depicted in Figure 1, ignoring pressure effects. A correlation between the ratios calculated from eq 6 and 7 and those given in Figure 1 is obtained if $A_{\alpha\alpha} \simeq 15A_{\alpha\beta}$. This amounts to a difference in the entropy of activation of about 5 eu, which is not unreasonable for the restriction on the methyl rotation involved in the transition state for the four-center process.[2]

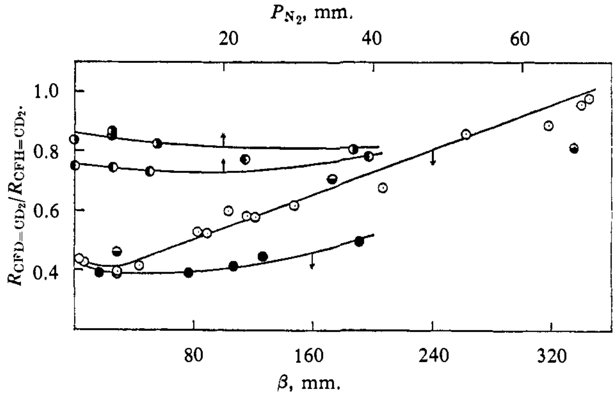

Figure 4. Plot of $R_{CFD=CD_2}/R_{CFH=CD_2}$ vs. β (mm) (see Figure 2) and pressure of added N_2: ○, $P_{TFA} + P_{d_6A} = 40$ mm, except for the two lowest pressures, at 240°; ●, $P_{TFA} + P_{d_6A} = 20$ mm at 240° (the apparent difference in the two sets of experiments is not readily explainable: note that at $\beta \leq 40$ mm, $P_{c\text{-}C_6F_{12}} = 0$); ◒, 40 mm of ketone, experiments at 300°; ◐, added N_2, 129–136°; ◑, added N_2, 236–243°. The N_2 curves have been displaced upward 0.4 unit for clarity.

The ratio $R_{CFD=CD_2}/R_{CFH=CD_2}$ (the 49/48 ratio) is shown as a function of pressure in Figure 4. Competitive unimolecular decompositions of vibrationally excited species have recently been discussed,[20] and our data show the expected general trend in the rate ratio with increasing pressure due to the increase of the average energy of the *reacting* molecules with pressure, which favors, relatively, the process with the higher critical energy. The experiments with added N_2 were at low ketone pressures (~0.5 mm with $d_6A/TFA \simeq 2$) so that reaction 1a, the stabilization step, was negligible in the absence of N_2.

We have depicted the curves in Figure 4 with shallow minima; see also the pressure dependence in Figure 1. We will adopt the following simplified picture: under conditions of considerable stabilization the lower energy end of the energy distribution for the initially formed "hot" molecules contributes less to the total HF elimination (*i.e.*, these molecules are longer lived and are preferentially stabilized by collision), and molecules that have lost energy to a quencher are essentially all stabilized. This causes the average energy of the *reacting* molecules to increase with pressure. Under conditions of less stabilization (lower pressure), molecules which have undergone a collision and which now constitute a second broader energy distribution centered about a lower average internal energy may still undergo elimination before further deactivation. Since $E_{\alpha,\beta}^* < E_{\alpha,\alpha}^*$, the probability of α,β vs. α,α elimination for a molecule in the second distribution is relatively greater than the probability in the first distribution.[21] At low pressures we may therefore see a relative

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(16) H. Okabe and J. R. McNesby, *J. Chem. Phys.*, 34, 668 (1961).

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

(18) (a) J. T. Bryant and G. O. Pritchard, *ibid.*, 71, 3439 (1967); G. O. Pritchard and R. L. Thommarson, *ibid.*, 71, 1674 (1967). See these references for definition of parameters and method.

(19) Both n and E^* were varied in each case; these represent the "best" fits. For several typical examples, see ref 6, 17, and 18.

(20) D. C. Tardy, B. S. Rabinovitch, and C. W. Larson, *J. Chem. Phys.*, 45, 1163 (1966).

(21) If we take an average internal energy E = 91 kcal mole^{-1} at 513°K, and assume that on the average 10 kcal mole^{-1} is removed by collision, from the RRK equation we see that $(k_{1b}/k_{1c})E = 91/(k_{1b}/k_{1c})E = 81 \approx 6$.

Table I. Data on the Cophotolysis of TFA and d_6A

		Products, moles × 10^8				Reactants		
Temp, °K	Time, sec	$CFH{=}CD_2$ + $CFD{=}CD_2$	CF_2HCD_3	$CF_2{=}CD_2$	49/48[a,b] ratio	P_{d_6A}, cm	P_{TFA}, cm	$P_{c\text{-}C_6F_{12}}$, cm
515	600	46.4	58.9	10.4	0.619	3.14	1.10	8.10
514	600	24.3	52.2	7.90	0.679	3.12	1.12	12.12
518	900	14.3	36.4	7.41	0.888	3.14	1.12	19.82
516	600	111	87.1	21.8	0.527	3.06	1.06	3.74
517	900	21.7	52.0	8.80	0.862	3.08	1.10	16.08
515	600	62.3	53.4	14.2	0.581	3.08	1.08	6.32
517	600	68.8	64.7	13.9	0.588	3.00	1.08	6.00
513	600	106	84.5	18.8	0.522	3.10	1.10	4.08
516	600	84.5	68.4	17.1	0.603	3.04	1.02	5.06
514	1200	12.4	45.1	6.70	0.962	3.04	1.06	21.46
514	1200	11.4	45.3	6.84	0.979	3.06	1.10	21.72
520	240	187	43.2	23.5	0.396	2.92	1.04	4.08
518	300	161	59.8	21.5	0.415	3.04	1.08	1.04
515	300	224	56.4	26.4	0.392	3.02	1.02	4.12
573	300	165	41.1	21.4	0.460	3.06	1.08	
573	1200	12.7	47.5	36.8	0.816	3.02	1.06	21.2
573	900	33.2	56.7	22.8	0.712	3.04	1.04	10.1
458	300	258	99.9	33.8	0.286	3.04	1.04	
439	300	266	106	37.7	0.260	3.08	1.00	
410	300	244	116	30.2	0.225	3.06	1.08	
554	300	187	41.4	24.4	0.437	3.06	1.04	
298	600	106	108	13.7	0.158	2.98	1.02	
384	420	274	154	34.9	0.208	3.00	1.06	
479	300	254	77.5	31.4	0.325	3.08	1.04	
517	600	727	17.8	78.0	0.423	0.73	0.25	
513	1200	799	9.96	96.8	0.432	0.37	0.16	

[a] No C^{13} isotope corrections have been made. There is a C_2 contribution to *m/e* 48 from *m/e* 47, $C_2FD_2^+$ which can arise by D-atom loss from C_2FD_3 and H-atom loss from C_2FHD_2. We estimate a downward correction of from 1 to 5% in our reported ratios, it being larger at low values of the 49/48 ratio. The reproducibility in the mass spectral analysis was about 1%. [b] A referee has pointed out that the 49/48 ratio shows a time dependence for runs at a particular temperature. This is so because time may be directly correlated with pressure. Increasing the pressure of $c\text{-}C_6F_{12}$ suppresses the photodecomposition of the ketones, so more extended times were used to build up sufficient product for accurate analysis. The last two runs in the table are included to demonstrate the independence of the ratio on time in the absence of $c\text{-}C_6F_{12}$. All of our data (ref 9, and M. J. Perona, Ph.D. Thesis, University of California at Santa Barbara, 1968) are in accord with this observation; *e.g.*, the two coincident results with a varying intensity factor (see Figure 1) had reaction times of 1200 and 7200 sec; P_{d_6A} = 1.8 cm and P_{TFA} = 0.21 cm in each case.[9]

enhancement of the α,β process which is minimized and ultimately swamped by the rapid deactivation of all but the most highly energized molecules. In general the nature of the competition between the two unimolecular processes as a function of pressure will depend upon the moderating environment ("strong," *e.g.*, ketone or $c\text{-}C_6F_{12}$, or "weak," *e.g.*, N_2, quenching), the separation in the critical energies for the two processes, and the temperature of the system, *i.e.*, the internal energy distribution and collision-free lifetimes of the originally formed "hot" molecules.

1,1-Difluoroethylene. This product was obtained in all of our experiments, and it is possible that there is a third mode of decomposition of the "hot" molecule formed in reaction sequence 1[22]

$$CF_2HCD_3^* \longrightarrow CF_2{=}CD_2 + HD \qquad (1d)$$

We[18a] had previously observed the formation of $CF_2{=}CH_2$ in the $CF_2HCH_3^*$ "hot" molecule system but concluded that its production was probably due to an impurity in the TFA reactant. Since the disproportionation of methyl radicals has never been observed

$$CD_3 + CD_3 \longrightarrow CD_2 + CD_4$$

it is unlikely that the $CF_2{=}CD_2$ is due to a combination of the two methylene species

$$CF_2 + CD_2 \longrightarrow CF_2{=}CD_2$$

and no C_2F_4 was observed in any case. A reaction such as

$$CF_2 + CD_3COCD_3 \longrightarrow CF_2{=}CD_2 + CD_3CDO$$

seems very unlikely and has no known precedent.

A plot from the data in Table I of $R_{CF_2=CD_2}/R_{CF_2HCD_3}$ *vs.* the inverse pressure coordinate used in Figure 2 is shown in Figure 5. The dependence is of the correct form for a "hot" molecule mechanism, but the nonzero intercept at infinite pressure indicates an additional source of $CF_2{=}CD_2$.[11,23] A plot of $R_{CF_2CH_2}/R_{CF_2HCH_3}$ is also given, which is based on our previous experiments[18a] with $CF_2HCH_3^*$. For the limited amount of data, the intercept is approximately zero.

Assuming that all the $CF_2{=}CD_2$ is produced in reaction 1d, a RRK treatment yields a critical energy of about 57 kcal $mole^{-1}$ for the elimination. A quenching efficiency for the composite bath gas of unity is obtained if the A factor is taken as $10^{12.9}$ sec^{-1}. A plot, corresponding to Figure 4, of $R_{CF_2=CD_2}/R_{CFH=CD_2}$ *vs.* pressure shows a similar positive slope in the 3–34 cm region, consonant with competing unimolecular reactions with E^* for reaction 1d > $E_{\alpha,\beta}^*$.

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[22] No $CF_2{=}CHD$ was observed, ruling out a possible α,α elimination of D_2.

[23] The value of the intercept may be adjusted by assuming different relative quenching efficiencies for the bath molecules. To be consistent we have retained the relative efficiencies used for the discussion of the α,α elimination; to do otherwise would cause our argument to appear to be contrived. Note in Figure 2 that the total elimination, and therefore the α,β elimination, has zero intercept. Since there is no reason to presuppose anything other than a "hot" molecule mechanism for the $CFH{=}CD_2$ formation, our choice of relative quenching efficiencies would appear to be justified.

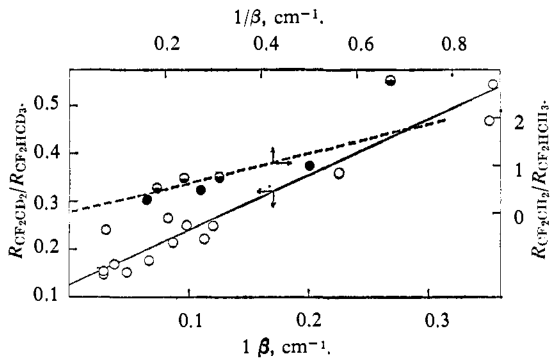

Figure 5. Plot of $R_{elimination}/R_{stabilization}$ *vs.* $1/\beta$ (see Figure 2): ○, $R_{CF_2=CD_2}/R_{CF_2HCD_3}$ at 240°; ● and ◒, $R_{CF_2=CH_2}/R_{CF_2HCH_3}$ at 145 and 188°, respectively.

The evidence that we have presented strongly suggests that the "hot" molecule $CF_2HCD_3^*$ may decompose by two, and probably three, competing unimolecular processes.[24] A complete understanding of this complex nonequilibrium system will further depend upon an analysis of the isotope effects.

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(24) A referee has observed that the disproportionation between any radical (CF_2H, CD_3, CD_2COCD_3, CF_2COCF_2H) in the system and CF_2H will yield CF_2 and that the reaction sequence

$$CF_2 + CD_2COCD_3 \longrightarrow (CF_2CD_2COCD_3)^* \longrightarrow CF_2CD_2 + COCD_3$$

accounts for the CF_2CD_2. We make the following points.

(a) Probably only the self-disproportionation *vs.* recombination of CF_2H's (k_d/k_r) is important, and is equal to 0.19;[6] values of k_d/k_r (to give CF_2) are for $CFH_2 + CF_2H = 0.06$,[6] for $CF_3 + CF_2H = 0.09$ (M. J. Perona and G. O. Pritchard, to be published), and for $CH_3 + CF_2H = 0$.[18a] The fate of the CF_2 has been difficult to establish unequivocally,[6] but fluoropropanes, from combination with monoradicals, have recently been observed (M. G. Bellas, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, 43, 1022 (1965); J. B. Hynes, R. C. Price, W. S. Brey, Jr., M. J. Perona, and G. O. Pritchard, *ibid.*, **45**, 2278 (1967); and to be published).

(b) A pathway involving CF_2 cannot be ruled out, and, where we conducted analysis for $C_2F_4H_2$, we find that $0.19C_2F_4H_2 > CF_2CD_2$. Similarly $0.19C_2F_4H_2 > CF_2CH_2$.[18a] However, the participation of acetonyl radicals cannot be assumed under all of our reaction conditions, although CF_2CD_2 is formed under all conditions. In our previous low-pressure experiments,[6] abstraction from the fluoroacetones was negligible up to 500°K, and the Arrhenius parameters are similar to those for d_6-acetone (with CD_3 or CF_2H), with $E^* = 10$–13 kcal mole^{-1}. At higher pressures abstraction is to be expected but not at room temperature; note the CF_2CD_2 production in Table I for the run at 298°K.

(c) Conversely, the decomposition of $(CF_2CD_2COCD_3)^*$ will not be favored at higher pressures.

Electronic States of Perimeter π Systems. IV.[1a] The Electronic Spectrum of [18]Annulene

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Abstract: It is shown that the electronic spectra of [18]annulene (VI) recorded so far have been incomplete and that there is a long-wave transition $B_{2u} \leftarrow A_{1g}$ ($^1L_b \leftarrow {}^1A$) at 13,000 cm^{-1}. This is in perfect agreement with theoretical predictions.

Recent experimental and theoretical investigations of the bridged [*n*]annulenes I,[2] II,[3] or III[4] (where $n = 2 + 4r$ satisfies the Hückel rule for closed-shell π perimeters) have shown that "aromatic" π-electron delocalization is not hampered noticeably even by the lack of coplanarity found for the peripheral π systems of I and II.[5] This conclusion is also supported by nmr and esr data.[6] In particular, the positions, intensities, and directions of polarization of the absorption bands in the electronic spectra of these compounds do not differ seriously from those predicted for the corresponding fully symmetrical all-*cis* models IV and V of D_{nh} symmetry by the standard many-electron treatments, *e.g.*, the Pariser–Parr–Pople (PPP) configuration interaction procedure.[7] This is shown in Table I, where the experimental data are compared with the results obtained from a PPP model of the type proposed by Longuet-Higgins and Salem.[8]

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